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Issued June 21, 1907.

U. S. DEPARTMENT OF AGRICULTURE,

BUREAU OF SOILS—BULLETIN No. 41.

MILTON WHITNEY, Chief.

THE ACTION OF WATER AND AQUEOUS SOLUTIONS UPON SOIL PHOSPHATES.

FRANK K. CAMERON AND JAMES M. BELL.

WASHINGTON:
GOVERNMENT PRINTING OFFICE.
1907.

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LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Soils,
Washington, D. C., March 22, 1907.

Sir: I have the honor to transmit herewith the manuscript of a technical article entitled "The Action of Water and Aqueous Solutions upon Soil Phosphates," by Messrs. Frank K. Cameron and James M. Bell, of this Bureau. It is a discussion of chemical reactions taking place constantly in the soil, and explains difficulties observed in soil management and fertilizer practice.

The article contains much valuable information which should be put at the disposal of the public interested in these lines of research. In accordance with your suggestion it has been gone over carefully with Assistant Secretary Hays, who authorizes me to state that he concurs in my recommendation for its publication.

Respectfully,

Milton Whitney,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

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THE ACTION OF WATER AND AQUEOUS SOLUTIONS UPON SOIL PHOSPHATES.

THE PHOSPHATES OF SOILS AND FERTILIZERS.

The literature of the phosphates is unusually voluminous, and it is very perplexing and contradictory. There is no class of inorganic compounds presenting so many apparent anomalies and at the same time having such importance in both pure and applied chemistry. But as voluminous and perplexing as is the chemical literature, and undoubtedly in large measure because of it, the agricultural literature of the phosphates far surpasses it in both respects, utterly defying attempts to systematize or rationalize the enormous number of observations recorded by students of the soil, plant physiologists, and agronomists. It is recorded that phosphates are especially useful on moor soils, on muck soils, on light soils, on heavy soils, for grain crops, for root crops, in the form of superphosphates, in the form of "floats" or other comparatively insoluble substances, especially when accompanied by green manures or similar decomposing organic matter; that they render soils acid; that they render soils alkaline. Many such statements might be cited quite as contradictory, which, while doubtless true for local conditions, are certainly too general and broad, because made with a lack of knowledge and appreciation of the chemical and physical properties of the phosphates. For some time past, therefore, the chemistry of certain soil phosphates has been under investigation in the laboratories of the Bureau of Soils, and these investigations have harmonized in a most gratifying manner the apparently chaotic results of numerous earlier studies. Much yet remains to be done before the chemistry of the phosphates can be regarded as altogether satisfactory, but it is believed that the researches of the Bureau have developed the fundamental relationships and characteristics of these substances to the point where, in the interest of both chemical research and practical field work, an orderly presentation of the results is demanded. Such is the purpose of the present bulletin.

The phosphates of lime, magnesia, iron, and alumina have a great and generally recognized importance in agriculture. It is in combination with the four bases cited that by far the major part of the phosphoric acid is held in the soil, and it is with these same bases that the phosphoric acid of commercial fertilizers is united.

A very large number of phosphates of these bases are recorded as having been found in nature and probably as many more as having been prepared artificially. Undoubtedly a large percentage of these supposed substances have a purely fictitious existence which would not pass scrutiny with modern criteria. Yet enough of them are definitely known to show that, under favorable conditions, phosphoric acid forms readily several phosphates with any single base, mixed phosphates of two or more bases, basic salts, and complex salts containing several bases and other acid residues than phosphoric acid. While any or all of these compounds might be present in a soil, it is very improbable, since, as will be shown in subsequent pages, very few of these compounds can be stable or persist long under soil conditions. Moreover, but very few of them have a wide distribution, and in fact it may be safely said that apatite is the only one which has any significance as a crystalline mineral component of the soil.

The mineral *apatite* is very widely distributed. It is present in most igneous rocks, and in lesser or greater amounts in practically all soils. The fact that it is so commonly found in soils has sometimes led to the belief that it is particularly resistant to weathering influences. It is much more probable, however, that the contrary is true, since apatite when finely divided is readily acted on by water and aqueous solutions, much more readily than the majority of soil minerals, and it seems probable that apatite is actually formed from solution under soil conditions, although laboratory efforts to prepare it in the wet way have so far proved unavailing. While the analyses of numerous specimens of apatite from many sources leave but little doubt as to the composition of this mineral, practically nothing definite is known as to its constitution. It is significant that all apatites so far examined, when powdered and treated with pure water freed from carbon dioxide, have given solutions which showed an alkaline reaction to such indicators as phenolphthalein or litmus, while the lime phosphates of the laboratory yield solutions acid to the indicators cited. That is, water extracts relatively more lime than phosphoric and hydrochloric (or hydrofluoric) acid from apatite, while with precipitated tricalcium and even more basic phosphates it extracts more acid than lime. It is of further significance that no crystalline substance of the composition of the hypothetically neutral tricalcium phosphate—$Ca_3(PO_4)_2$—has yet been found in nature or recognized in the laboratory.

The presence of dissolved carbon dioxide greatly increases the solubility and decomposition of apatite. In such case again, much more lime than acid is extracted. For instance, a chlorapatite was ground fine in a ball mill, suspended in water in a closed container at room temperature (25° to 30° C.). Carbon dioxide was constantly passed through the solution for seven days, the pressure of the vapor over the solution being maintained at about 21 pounds. At the end of the period analysis of the supernatant solution showed 0.0378 gram lime (CaO), 0.0096 gram phosphoric acid (P_2O_5), and 0.0026 gram hydrochloric acid (HCl) per liter of solution, or, in terms of reacting weights, CaO:P_2O_5:HCl as 10:1:1.

Large deposits of massive apatite are found in a few localities in America and Europe and have been mined for the raw material in the preparation of superphosphates. In this country at the present time the rock phosphates of the South have practically superseded apatite in fertilizer manufacture and the latter occupies an insignificant position in the trade.

A magnesium fluo-phosphate corresponding to apatite is known as *wagnerite*, and a ferrous salt, *triplite*, is also known, but they seem to be much rarer than their calcium analogies and are probably of little importance as soil minerals. The diphosphates of calcium, *monetite* ($CaHPO_4$) and *brushite* ($CaHPO_4.2H_2O$), while found in nature as mineral components of guano, could not long persist under soil conditions, since they are not stable in contact with solutions as dilute as the normal soil water, and would soon be transformed to more basic phosphates.

It is reasonable to suppose that some of the phosphoric acid of the soil is combined with lime in a manner identical with or very similar to the *rock phosphates* of South Carolina, Florida, and Tennessee. This substance, like the *capriolites*, *osteolites*, *phosphorites*, etc., found in more limited quantities in various parts of the world, seems to be an amorphous body containing lime and phosphoric acid in proportions varying more or less from that required by the formula for tricalcium phosphate, and always mixed with some calcium carbonate. Recent investigations have shown indubitably that these phosphatic bodies are members of a series of solid solutions of phosphoric acid in lime, the limiting solutions of the series being pure calcium hydroxide at one end and at the other end a solid solution very close in composition to dicalcium phosphate.

The ferrous phosphate, *vivianite* ($Fe_3(PO_4)_2.H_2O$), and the basic aluminum phosphate, *wavellite* ($3Al_2O_3.2P_2O_5.12H_2O$), are fairly widely distributed minerals, and both occur under conditions which suggest their possible deposition from aqueous solution; but the opinion of some authors that these are soil minerals in the sense of usually being present is yet lacking any satisfactory demonstration. Their importance as a source of phosphoric acid in the soil is certainly small.

The sources of phosphatic fertilizers of present commercial importance are (1) phosphate rock, (2) bones and bone preparations, (3) basic slags, and (4) guanos.

The *phosphate rock* of South Carolina, Florida, and Tennessee is a mixture containing phosphoric acid, lime, and lime carbonate in somewhat varying proportions. The percentage of phosphoric acid (P_2O_5) present varies from about 25 to 30, the Tennessee rock probably averaging somewhat higher than that from the other localities. Constitutionally the substance must now be regarded as a mixture of lime carbonate and a solid solution containing phosphoric acid and lime. The finely powdered material, when shaken with pure water, gives usually a solution alkaline to the ordinary indicators, but samples richer in phosphoric acid frequently give a distinctly acid solution. Phosphate rock is used as a fertilizer in two forms, as the ground rock, and as "floats," a very finely comminuted product, the latter being regarded as much superior. The value of rock phosphate as a fertilizer has long been a much mooted question among agriculturists. Many have held that it has but a slight value and is in no degree to be compared to the soluble superphosphates. An increasing weight of authority now holds, however, that, with proper conditions and methods of cultivation, "floats" are little if any inferior to superphosphates, except in special cases where an immediate or very rapid response is desired. The solubility and decomposition of rock phosphate are much increased and hastened by the presence of carbon dioxide in the water, and it is held that if organic matter, especially green manures, be thoroughly incorporated in the soil with the phosphate the carbon dioxide and possibly other acids resulting from the decomposition of the organic matter so increase its solubility as to make it compare very favorably with the rapidly soluble superphosphates. It is somewhat difficult to draw definite conclusions regarding this matter from field experiments, since many of the favorable results are probably due directly to the decomposition of the organic matter rather than to the dissolved phosphates.

Ground bone, or *bone meal*, is very similar to rock phosphate, containing about the same percentage of phosphoric acid, but is generally preferred because it contains some nitrogenous matter which is itself useful as fertilizer. *Steamed bone meal* is very similar, except that the fatty material and some of the nitrogenous material have been removed by superheated steam before grinding. It is generally preferred to the raw bones, since the fatty matter is supposed to retard the solubility and decomposition of the phosphatic material. *Bone ash* and *boneblack*, though containing a higher percentage of phosphoric acid, 30 to 40 per cent, is but little used as a direct fertilizer, but mainly as a raw product in the manufacture of superphosphate.

Superphosphate, sometimes known as acid phosphate, monocalcium phosphate, one lime phosphate, or soluble lime phosphate, is prepared from rock phosphate or bone phosphates by treatment with a solution of sulphuric acid of density about 1.55. It is far more soluble than the other phosphates of lime. The sulphuric acid, usually "chamber acid," approximately a 60 per cent solution, is taken in a quantity somewhat less than that required to convert into sulphate all the lime in excess of that required by the phosphoric acid for the formation of the monophosphate. This is necessary, since it has been found that, if the theoretically required amount of acid be used, the resulting product is of a pasty consistency difficult to handle and so acid as to be considered harmful to vegetation. The amount of water in the sulphuric acid solution is approximately that required for the solid monocalcium phosphate ($CaH_4(PO_4)_2.H_2O$) and for the conversion of the sulphate formed into gypsum ($CaSO_4.2H_2O$). On standing, however, some water is gradually absorbed from the air and the undecomposed phosphatic material reacts with the monophosphate to form some of the much less soluble dicalcium phosphate. This process is known as "reversion." It is of course augmented by the presence of impurities, like the oxides of iron and alumina, which themselves form very slightly soluble phosphates. In the soil the process of reversion must be very rapid and complete. This is shown by the fact that the aqueous extract of soils treated with monocalcium phosphate, even in quantities far in excess of those actually used in fertilizer practice, are in general no richer in phosphoric acid than untreated soils. It seems probable, therefore, that the principal advantage in the use of the readily soluble superphosphate is to obtain a good distribution in the soil, or to realize for a brief time a relatively high concentration of phosphoric acid in the soil water; and, further, that the addition of phosphates must have some other function than merely increasing the supply of potential plant nutrient in the soil.

Basic slag, or *Thomas slag*, is the discarded lining of converters which has absorbed the phosphorus from the pig iron in the manufacture of iron and steel. It is similar in general respects to a low-grade rock phosphate, containing from 15 to 20 per cent phosphoric acid. Its efficiency seems to depend mainly on the degree of fineness to which it is ground and the method of application, being especially valuable when used with green manures. It is interesting chemically because the slag sometimes contains well characterized crystals of a tetracalcium phosphate[a] ($Ca_4P_2O_9$). Tetracalcium phosphate has not been, and probably can not be, made in the wet way, and is therefore unstable in aqueous solutions. Slag products containing iron, aluminum, and phosphoric acid under various names, such as *redondite*, are used to some extent as fertilizers. Their efficiency seems to be greatly augmented by the addition of lime or decaying organic matter. They have but small commercial importance in the United States at present.

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[a] Otto, Chem. Zeit., **11**, 255 (1887); Wiley and Krug, Jour. Anal. Chem., 5, 685 (1891).

Guano is the excrement and remains of sea fowls, which have accumulated in certain regions on the coast of South America or on islands in the Caribbean Sea. Bat guano is similar material taken from caves. Guanos from very arid regions are rich in nitrogenous material, while those from more humid regions are valuable mainly for the phosphates which they contain. At one time the principal commercial fertilizers, guanos have now but little importance in the trade. Phosphatic guanos containing from 10 to 35 per cent phosphoric acid are occasionally used still for direct application to the soil, but more often as a raw material for the manufacture of superphosphates.

It is probable that by far the greater part of the phosphoric acid of the soil is held there by ferric oxide with more or less alumina. But it is very improbable that the soil contains normally any definite compound of iron or aluminum with phosphoric acid, as the concentration of phosphoric acid in solution necessary for the stable existence of any definite phosphate of iron in contact with the solution is far greater than would ever occur in the soil water. It seems most probable that the phosphoric acid is held mainly as a solid solution and possibly to some extent absorbed by purely surface forces. But no matter in what forms the phosphoric acid may exist in the soil, the resulting soil solution is always quite dilute[a], even though the actual quantity of phosphoric acid in the soil may be very high. Few, if any, satisfactory results have yet been obtained for the solution as it actually exists in place in the soil, but the results of work on aqueous extracts of soils and percolation experiments[b] show that the concentration of the soil solution in phosphoric acid must be quite low (probably about 5 or 6 parts per million), that it varies but little with different soils or with the total amount that may be present in the solid components of the soil. When a phosphate, no matter how soluble, is added to the soil, experiment shows that it is very promptly absorbed and "fixed" and the concentration of the soil water is not sensibly affected except possibly for a very brief period. It would seem, therefore, that the function of phosphatic fertilizers is something other than adding to the store of "available" plant food.

The explanation of these facts is apparent from the investigations described in the following pages.

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[a] See Johnson, "How Crops Feed," pp. 309 et seq., 1890; Whitney and Cameron, Bul. No. 22, Bureau of Soils, U. S. Dept. Agr. (1903).

[b] See especially Schreiner and Failyer, Bul. No. 32, Bureau of Soils, U. S. Dept. Agr. (1906).

ACTION OF WATER ON THE PHOSPHATES OF CALCIUM.

The contradictory nature of many of the statements in the literature of the phosphates of calcium arises from several different causes. There is a very general misconception of the action of water upon the different compounds of lime and phosphoric acid. Many attempts have been made to determine the solubility of these compounds in water—a "solubility" which depends upon the ratio of water to salt in the mixture. In all cases where one of these compounds is placed in contact with water, the ratio of phosphoric acid to lime becomes greater in the solution than it was in the original solid; hence the solid phase wholly or partially undergoes a decomposition. A second cause of the wide variation in different results is the uncertainty as to the nature of the solid whose solubility was to be determined. For instance, it will be shown subsequently in this paper that the so-called tricalcium phosphate ($Ca_3(PO_4)_2$) is not a definite chemical compound, but is one of a series of solid solutions of lime and phosphoric acid. A solid having the composition expressed by the above formula would change its composition upon contact with water to that of another of the series of solid solutions of which series it is a member. The behavior of this tricalcium phosphate at ordinary temperatures and in contact with water or aqueous solutions does not exclude, however, the possibility that under other conditions, such as high temperature, there may be a compound of the above formula which may exist over a considerable range of concentration in a molten magma. A third possible source of error in the results upon the "solubility" of the phosphates of calcium very probably rises from the extreme slowness with which equilibrium conditions are attained in dilute solutions.

Before any detailed consideration of the various phosphates of calcium is undertaken, a few well-known examples will be reviewed which in some respects resemble the case under special consideration. Water decomposes the chloride and nitrate of bismuth, both of which are well-defined crystalline compounds. In the case of the chloride, the reaction may be represented by the reversible equation

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + HCl,$$

and there remains in solution the hydrochloric acid formed in the reaction and some of the bismuth oxychloride which the acid solution dissolves. If the solution should be removed and more water added to the solid, there will result more bismuth oxychloride, a compound in which the ratio of bismuth to chlorine is greater than in the original bismuth trichloride. The above reaction may also be shown to be reversible, for by adding more hydrochloric acid to the solution, the bismuth oxychloride tends to dissolve, while on the other hand addition of more water causes more of the bismuth to precipitate from solution as the oxychloride. Another well-known example is the action of water upon ferric chloride according to the scheme

$$FeCl_3 + H_2O \rightleftharpoons Fe(OH)_3 + HCl,$$

and in the solution containing hydrochloric acid there remains most of the original quantity of iron, *but not all of it.* The rest of the iron forms ferric hydroxide which precipitates. This reaction, too, is reversible, for the addition of more hydrochloric acid to the solution tends to dissolve the ferric hydroxide, while the addition of water tends to increase the quantity of ferric hydroxide as precipitate. It is well known that more acid is required to dissolve ferric hydroxide in suspension than would be indicated by the formula $FeCl_3$, supposing that the salt went into solution as such. Another example of this hydrolysis is the acid solution which is obtained when the sulphate of zinc, mercury, or cadmium is dissolved in water, an acidity which can not be removed by adding the hydroxide of the metal to the solution.

Monocalcium phosphate.

The solubility and decomposition of monocalcium phosphate by water have been subjects of a large amount of experimental research, and for an understanding of the modern views on this subject a review of the literature becomes necessary.

Erlenmeyer [a] has published several papers on the subject, in the last of which he concludes that monocalcium phosphate when added to water in greater proportion than 1:700 was decomposed with the formation of solid dicalcium phosphate, the solution containing more acid than corresponds to the formula $CaH_4(PO_4)_2$. A very different ratio has been given by other authors. Wattenberg [b] has stated that one part of the salt dissolved without other change in 144 parts of water, and Otto [c] has affirmed that one part of the phosphate in 25 parts of water suffers no decomposition. These conclusions are considered incorrect by Stoklasa,[d] who has employed a preparation containing but little free phosphoric acid, and has found that one part of the salt dissolves in 200 parts of water without decomposition.

It has further been shown that in several cases the material believed to have the composition $CaH_4(PO_4)_2.H_2O$ contained an excess of free phosphoric acid, the amount of water necessary for the disappearance into solution of the material depending very greatly upon the quantity of free acid present. Erlenmeyer [a] and Stoklasa [b] have both shown that the pure substance is not hygroscopic, and that in the presence of free phosphoric acid there is a rapid increase in weight when that substance stands in moist air. The preparations of Packard [c] and of Birnbaum [d], which were very hygroscopic, contained in all probability some free acid.

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[a] Jahresb., 1857, 145; Verhandlung d. Math. phys. Klasse d. K. bayer. Akad., 1872, 269; Ber., **9**, 1839 (1876).

[b] Zur Bestimmung der löslichen Phosphorsäure in Superphosphaten, 1870; ref. in Stoklasa, Landw. Vers.-Stat., **38**, 212 (1891).

[c] Zeit. angew. Chem., **20**, 208 (1887).

[d] Listy Chem., **13**, 203, 240, 273 (1890); ref. in Jour. Chem. Soc., **58**, 695 (1890); Landw. Vers.-Stat., **38**, 197 (1891); Zeit. anorg. Chem., **1**, 307 (1892).

The very wide differences in the results obtained in the above papers indicate that the method employed in the determinations was questionable. If the phenomenon were one of true solubility, the presence of small quantities of free phosphoric acid would not be expected to cause such wide variations in the results of different experimenters, and also the solubility would not depend upon the ratio in which the salt and water are mixed. As the quantity of lime and of phosphoric acid in solution do not stand in the same ratio as in the original salt, and as the ratio depends upon the temperature and upon the relative amounts of salt and water which were mixed originally, it is apparent that we are dealing not with a true solubility phenomenon but with the phenomenon of hydrolysis, similar to the cases which have been reviewed above.

In the following table Stoklasa has given the composition of the solution resulting when monocalcium phosphate and water are mixed in varying proportions at room temperature (10° to 20° C.). It will be seen that as the quantity of water is increased the absolute quantity of lime and of phosphoric acid dissolved increases somewhat, but that the concentration of the solutions falls very rapidly.

TABLE I.—*The composition of solutions (10° to 20° C.) obtained when monocalcium phosphate and water are mixed in varying proportions.*

Mixture originally taken.		In solution.	
$CaH_4(PO_4)_2.H_2O$.	H_2O.	Lime.	Phosphoric acid.
Gram.	*Grams.*	*Gram.*	*Gram.*
1	1	0.1624	0.4902
1	25	.1900	.5259
1	50	.2063	.5486
1	75	.2148	.5598
1	150	.2180	.5642
1	200	.2236	.5668

Many of the modern writers on this subject are correct in the opinion that when monocalcium phosphate is added to water there is a change into some of the solid hydrated dicalcium phosphate

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[a] Verhandlung d. Math. phys. Klasse d. k. bayer. Akad., 1872, 269.

[b] Listy Chem., **13**, 203, 240, 273 (1890); ref. in Jour. Chem. Soc., **58**, 695 (1890); Landw. Vers.-Stat., **38**, 197 (1891).

[c] Zeit. Chem. (2), **7**, 137 (1871).

[d] Ber., **6**, 898 (1873).

($CaHPO_4.2H_2O$)—at higher temperatures to the anhydrous salt ($CaHPO_4$)—and also to a solution in which the ratio of phosphoric acid to lime is greater than in the original monocalcium phosphate. This may be indicated partially by the equation,

$$CaH_4(PO_4)_2.H_2O + H_2O = CaHPO_4.2H_2O + H_3PO_4,$$

the free phoshoric acid in aqueous solution carrying with it some of the dicalcium phosphate. This reaction is quite similar to the reaction which has been cited above, where water caused a change of bismuth trichloride to bismuth oxychloride. In the present case the addition of much water will cause the reaction to go to the right, i. e., to the change of all the monocalcium phosphate to dicalcium phosphate, and to phosphoric acid in solution, which carries a considerable quantity of the lime phosphate. The addition of phosphoric acid to the solution will cause solution of more dicalcium phosphate.

By mixing water and monocalcium phosphate in varying proportions Joly[a] has found that the resulting solid phase was dicalcium phosphate, while the solution contained both lime and phosphoric acid. The experimental data show that the solution is richer in phosphoric acid than it would be if monocalcium phosphate went into the solution as such. Where quantities, 4.02 to 49.01 grams, of the salt have been added to 100 grams of water, the free phosphoric acid in solution (supposing the lime to exist in solution as monocalcium phosphate) increases from 0.106 to 5.645 grams. If the quantity of monocalcium phosphate added to 100 grams of water exceeds 65 grams, the excess of salt undergoes no decomposition, and also the composition of the solution remains unchanged for each further addition of the salt. Under these conditions, therefore, there are two solid phases, monocalcium phosphate and dicalcium phosphate, and when the temperature is fixed the resulting solution is constant in composition. The "free" phosphoric acid in this constant solution (assuming the lime to be combined as monocalcium phosphate) was 8.06 grams in 100 grams of water. As no temperature has been recorded, a comparison with results of more modern work is of questionable value. However, it would be well to point out that Cameron and Seidell[b] have shown that where both monocalcium phosphate and dicalcium phosphate are present as solids the quantity of "free" phosphoric acid (P_2O_5) is about 120 grams per liter of solution at 25° C.

The composition of solids and solutions resulting from the mixing of monocalcium phosphate and water in various proportions at 100° has been determined by Viard.[c] In every case it was found that the solid was anhydrous dicalcium phosphate, which differs from the hydrated salt by being insoluble in acetic acid. The compositions of the various solutions as given by the author are contained in the following table:

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[a] Compt. rend., **97**, 1480 (1883).

[b] Jour. Am. Chem. Soc., **27**, 1503 (1905).

[c] Compt. rend., **127**, 178 (1898).

TABLE II.—*The composition of solutions (100° C.) obtained when monocalcium phosphate and water are mixed in varying proportion.*

P_2O_5 in 1,000 grams solution.	CaO in 1,000 grams solution.	Density.
Grams.	*Grams.*	
4.91	1.63	1.0016
8.67	2.40	1.093
19.34	4.40	1.01
35.60	6.96	1.03
136.16	23.90	1.14
222.30	37.50	1.24

These results have been calculated to give the quantity of each component in a liter of solution, and have been platted in the accompanying diagram (fig. 1).

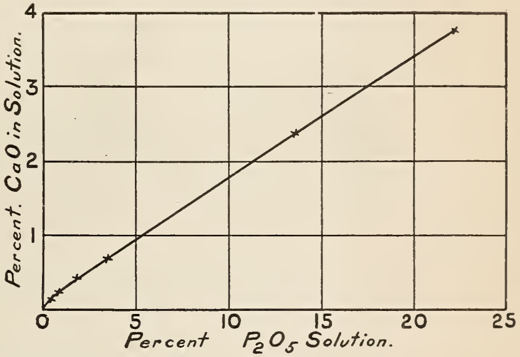

FIG. 1.—Diagram showing the quantities of lime and phosphoric acid in solutions, in equilibrium with dicalcium phosphate, at 100° (Viard).

Dicalcium phosphate.

When water is added to a dicalcium phosphate there is a decomposition into an amorphous solid and a solution. The composition of the solid shows a greater ratio of lime to phosphoric acid than the original dicalcium phosphate. Many authors[a] have shown that this change takes place, although nearly all have considered the resulting solid to be tricalcium phosphate.

Boiling water has been shown by Millot to act in a double rôle upon hydrated dicalcium phosphate. It is partially changed to an amorphous solid supposed to be tricalcium phosphate, free phosphoric acid going into solution and carrying with it some lime; the rest of the dicalcium phosphate is changed from the hydrated form to the anhydrous salt. This latter observation has been confirmed by Viard.[b]

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[a] Wattenberg, Jour. f. Landw., **27**, 27 (1879); Millot, Bul. Soc. Chim. (2), **33**, 194 (1880); Delattre, Bul. Soc. Chim. (2), **35**, 358 (1881); Stoklasa, Landw. Vers.-Stat., **38**, 401 (1891); Joly and Sorel, Compt. rend., **118**, 738 (1894); Barillé, Rép. Pharm., 1897, 529; ref. in Chem. Centr., **69**, I, 434 (1898); Joffre, Bul. Soc. Chim. (3), **19**, 372 (1898); Rindell, Compt. rend., **134**, 112 (1902); et al.

[b] Compt. rend., **127**, 178 (1898).

The experiments of Dellatre also show that dicalcium phosphate undergoes a decomposition when treated with boiling water. He considers that insoluble tricalcium phosphate is formed and that monocalcium phosphate passes into solution.

Joly and Sorel, after successive extraction of 1 part of dicalcium phosphate with 100 parts of water, found that the water extracts were decidedly acid, and that the solid became gelatinous and of the composition $Ca_3(PO_4)_2.1/2H_2O$. These authors have also determined the composition of the solid residue after various quantities of dicalcium phosphate had been extracted with equal quantities of water. As the ratio of salt to water increases, the composition of the solid residue approximated more and more closely to that of dicalcium phosphate. As will be shown from the work of Rindell, the solid was probably composed of different proportions of two solid phases, one of which was dicalcium phosphate. Joly and Sorel have ascribed the formula $Ca_3(PO_4)_2.8CaHPO_4.2H_2O$ to one of these solid residues, but it now seems probable that this is a mixture of two solid phases, or is one of a series of solid solutions.

With very large quantities of water the decomposition of monocalcium phosphate may proceed even farther than dicalcium phosphate. This has been recorded by Joffre, who has observed that the solid residue was composed of dicalcium phosphate and tricalcium phosphate.

The action of water upon different quantities of dicalcium phosphate has been determined at 18° C. by Rindell. To insure equilibrium conditions the electrical conductivity of the solutions was determined at intervals, and it was found that over ten days was required for the solution to reach a constant conductivity. The solutions obtained by adding 6, 10, 12, or 14 grams of dicalcium phosphate to 1 liter of water were all found to have the same conductivity. The analyses of some of the solutions gave the following results:

TABLE III.—*The composition of solutions obtained when dicalcium phosphate and water are mixed in varying proportion 18° C.*

Solid added to one liter water.	CaO per liter.	P_2O_5 per liter.
Grams.	*Gram.*	*Gram.*
2	0.0725	0.303
10	.0732	.314
14	.0737	.315

As the solution became constant in composition when quantities of dicalcium phosphate greater than 6 grams were added to one liter of water, it follows that the solid in equilibrium with the solution was composed of two solid phases, one of which was dicalcium phosphate.

With quantities less than 6 grams to one liter, the conductivity of the solutions decreased with decreasing quantities of dicalcium phosphate.

Very recently Buch [a] has investigated the decomposition of dicalcium phosphate by water. In his experiments, dicalcium phosphate was subjected to a continuous leaching by adding water to the solid, and, after removing the solution, adding more water. In 53 successive extractions made in this way the author has accomplished a complete transformation of dicalcium phosphate to tricalcium phosphate, and concludes his paper as follows: "Whether this stage is the limit of the decomposition, or whether the transformation may be carried farther to a basic compound, so that tricalcium phosphate is to be considered as a stable intermediate step, it is difficult at the present time to decide. Several facts, especially the numerous basic phosphoric acid compounds occurring in nature, are evidence for the latter alternative."

Tricalcium phosphate.

The composition of the solid resulting from the decomposition of a phosphate of lime depends upon the composition of the solution. If the solution is very rich in phosphoric acid the solid is monocalcium phosphate. If water be now added to the system, the solid is dicalcium phosphate, and if the solution be very greatly diluted there is a decomposition to a solid less rich in phosphoric acid than dicalcium phosphate. This decomposition may even go so far as to yield a solid less rich in phosphoric acid than would be represented by the formula $Ca_3(PO_4)_2$.

By determinations of the weight of the solid residue from the evaporation of pure water which had stood in contact with various phosphates of lime, Maly and Donath [b] have found that 2.36 parts of gelatinous tricalcium phosphate dissolve in 100,000 parts of water, that 2.56 parts of the ignited phosphate or 3 parts of bone powder dissolve in 100,000 parts of water.

By successive extractions of so-called tricalcium phosphate by boiling water Warington [c] has obtained a product more basic than tricalcium phosphate. This is shown by the following tables. Table IV gives the analysis of the solid obtained after twelve extractions, the water remaining in contact with the solid for two hours each time; and Table V gives the composition of the solid obtained after ten extractions with boiling water, which remained in contact with the solid for four hours each time.

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[a] Zeit. anorg. Chem., **52**, 325 (1907).

[b] Jour. prakt. Chem., **115**, 413 (1873).

[c] Jour. Chem. Soc., **26**, 983 (1873).

TABLE IV.—*The changes in the composition of lime phosphate consequent on successive extractions with water.*

Constituent.	Composition of original phosphate of lime.	Ratio of lime to phosphoric acid in solution after first extraction.	Composition of the precipitate after 12 extractions.
	Per cent.	*Per cent.*	*Per cent.*
Lime	54.37	25.87	56.33
Phosphoric acid	45.63	74.13	43.67

TABLE V.—*The changes in the composition of lime phosphate consequent on successive extraction with boiling water.*

Constituent.	Composition of original phosphate of lime.	Ratio of lime to phosphoric acid in solution after first extraction.	Composition of the precipitate after 10 extractions.
	Per cent.	*Per cent.*	*Per cent.*
Lime	54.78	19.09	56.69
Phosphoric acid	45.22	80.91	43.31

In another experiment it was shown that the solids obtained after the first extraction and after subsequent extractions showed very different solubilities, the content of the solution in phosphoric acid calculated as tricalcium phosphate being 1 in 4,651, while after a later extraction the apparent solubility was 1 in 657,000. For the solid residue remaining after many extractions Warington has proposed the formula $3Ca_3(PO_4)_2.Ca(OH)_2$.

These experiments show that tricalcium phosphate, like monocalcium and dicalcium phosphate, is unstable in contact with water, and, like them, gives a solution in which the ratio of phosphoric acid to lime is greater than in the original solid, the solid residue becoming more and more basic, on continued extraction with water. The solid residue also becomes decreasingly soluble on repeated treatment with water. The following sentence is quoted from Warington's paper: "Since it appears that all phosphates of calcium are unstable under the continued action of pure water, it seems probable that a more exact examination of natural phosphates would show that many phosphates now regarded as tricalcic are, in fact, of a more basic nature."

The formula $3Ca_3(PO_4)_2.Ca(OH)_2$ given to the solid residue by Warington appears to be confirmed by Aeby,[a] who found that the composition of bone phosphate may be expressed by the formula $3Ca_3(PO_4)_2.CaO$. This latter contention is disputed by Wibel,[b] who holds that the composition of bone phosphate is not constant.

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[a] Jour. prakt. Chem., **113**, 308; **114**, 169 (1872); **115**, 37 (1873).

[b] Jour. prakt. Chem., **117**, 113 (1874).

The three-component system—lime, phosphoric acid, water.

From the literature which has been cited it is evident that monocalcium phosphate, dicalcium phosphate, and the so-called tricalcium phosphate are all unstable in the presence of pure water, and that they all break down to solids which contain relatively more lime than the original solids. All the resulting solutions contain both lime and phosphoric acid, the ratio of acid to lime being greater in the solution than the original solid. This has been recognized by Causse [a] in his determination of the solubility of dicalcium and of tricalcium phosphates in various solutions of phosphoric acid. The solid phosphate was added to the solution until no more would dissolve, and after standing 24 hours the supernatant liquid was analyzed for lime and phosphoric acid. As no temperature has been recorded, and as it has been found recently that one day is not sufficient for attaining equilibrium conditions, the results can not be compared with those obtained more recently. In the following tables the determinations of Causse have been recalculated:

TABLE VI.—*Tricalcium phosphate added to phosphoric acid solutions.*

CaO per liter.	P_2O_5 per liter.	CaO per liter.	P_2O_5 per liter.
Grams.	*Grams.*	*Grams.*	*Grams.*
17.0	65.9	55.2	247.3
32.2	129.4	60.9	298.9
41.7	185.9	66.6	350.7

TABLE VII.—*Dicalcium phosphate added to phosphoric acid solutions.*

CaO per liter.	P_2O_5 per liter.	CaO per liter.	P_2O_5 per liter.
Grams.	*Grams.*	*Grams.*	*Grams.*
17.7	86.8	48.9	239.4
29.5	126.1	55.2	291.9
38.3	181.6	62.2	345.1

Each of the solutions described by the above tables was then heated to 100° C. for one hour. From the last two solutions of the former table and from all the solutions of the latter table a solid separated, which on investigation proved to be dicalcium phosphate.

The composition of aqueous solutions containing lime and phosphoric acid and of the solids in equilibrium with them at 25° has recently been investigated by Cameron, Seidell, and Bell.[b] The results obtained in these investigations are given in the following table, and the concentrations of the solutions are represented graphically in the accompanying diagram (fig. 2).

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[a] Compt. rend., **114**, 414 (1892).

[b] Jour. Am. Chem. Soc., **27**, 1503, 1512 (1905).

TABLE VIII.—*Composition of aqueous solutions containing lime and phosphoric acid at 25° C.*

P_2O_5 per liter solution.	CaO per liter solution.	Ratio P_2O_5/CaO in solid phase.	Solid phase in contact with solution.
Grams.	*Grams.*		
0.012	0.789	0.4	Solid solution.
.013	.587	.4	Do.
.015	.034	.8	Do.
.088	.049	.9	Do.
.109	.062	.9	Do.
.381	.145	1.0	Do.
.662	.232	1.1	Do.
.773	.291	1.1	Do.
1.108	.400	1.1	Do.
1.516	.544	1.2	Dicalcium phosphate.
3.66	1.58	1.2	Do.
5.75	2.42	1.2	Do.
8.16	3.42	1.3	Do.
12.82	5.01	1.3	Do.
16.52	6.51	1.2	Do.
19.96	7.61	1.3	Do.
22.39	7.48	1.4	Do.
23.37	8.10	1.3	Do.
36.14	11.57	1.3	Do.
41.24	12.88	1.5	Do.
59.35	18.77	1.3	Do.
63.03	19.25	1.4	Do.
75.95	23.31	1.2	Do.
79.10	23.69	1.5	Do.
109.8	32.41	1.3	Do.
129.8	35.90	1.3	Do.
139.6	39.81	1.3	Do.
142.7	40.89	1.3	Do.
154.6	43.82	1.3	Do.
191.0	49.76	1.4	Do.
216.5	55.52	1.3	Do.
234.6	59.40	1.4	Do.
279.7	70.31	1.5	Do.
351.9	72.30	2.4	Monocalcium phosphate.
361.1	69.33	2.4	Do.
380.3	65.46	2.4	Do.
395.1	63.53	2.4	Do.
419.7	59.98	2.6	Do.
424.6	59.25	2.4	Do.
428.0	57.74	2.6	Do.
451.7	53.59	2.2	Do.
475.3	48.78	2.2	Do.
505.8	44.52	2.3	Do.
528.9	41.86	2.4	Do.
538.3	39.89	2.5	Do.

The results of the analyses of the solid phases show that there is a series of solutions in equilibrium with a solid in which the ratio of phosphoric anhydride to lime is about 2.5. The ratio of phosphoric anhydride to lime in monocalcium phosphate is 2.5. Another series of solutions is in equilibrium with a solid in which the ratio of phosphoric anhydride to lime is about 1.3, in which ratio phosphoric anhydride and lime are present in dicalcium phosphate. A third series of solutions is in equilibrium with a series of solids in which the ratio of phosphoric anhydride to lime is variable (from 1.1 to 0). In the diagram the first two series of solutions have been represented. It is evident that at some concentration it is possible to have the two phosphates of lime (monophosphate and diphosphate) present in equilibrium with a solution. This concentration may be determined by reading from the diagram the content of lime and of phosphoric acid in the solution which is represented by the intersection of the two curves. This concentration is approximately 77 grams of lime and 317 grams of phosphoric anhydride per liter of solution, the solution having a specific gravity of approximately 1.29 as compared with water at the same temperature.

The two dotted lines A and B on the plate indicate the systems in which the ratio P_2O_5 : CaO is the same as in the compounds $CaHPO_4$ and $CaH_4(PO_4)_2$, respectively. The line A does not cut the curve representing the solution equilibrium with solid dicalcium phosphate, and hence it is impossible at the temperature 25° to obtain in equilibrium with a solid of the composition $CaHPO_4.2H_2O$, a solution containing lime and phosphoric acid in the same ratio. On the other hand, the line B cuts the curve representing the solution in equilibrium with monocalcium phosphate, but the point of intersection represents a solution supersaturated with respect to dicalcium phosphate. It is therefore possible, theoretically, to obtain a solution of monocalcium phosphate in equilibrium with solid monocalcium phosphate. Such a solution would, however, be unstable with respect to dicalcium phosphate.

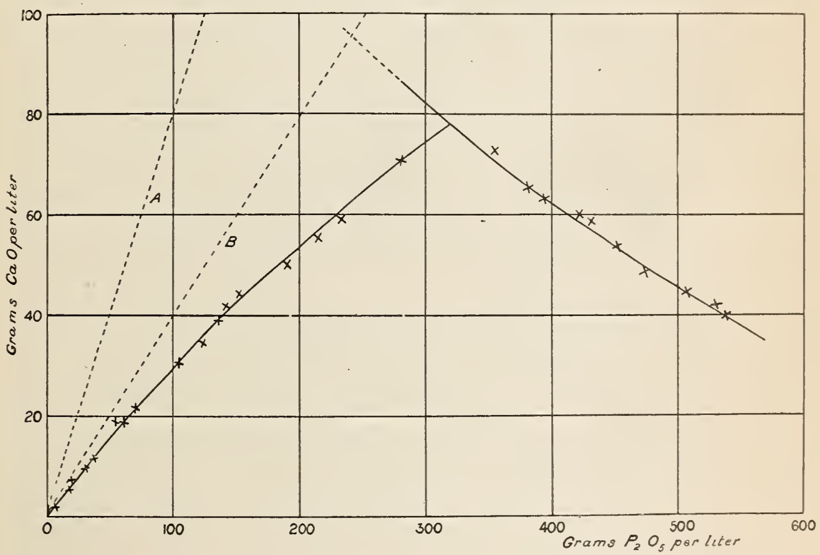

FIG. 2.—Diagram showing the quantities of lime and phosphoric acid in solutions in equilibrium with the crystalline phosphates of lime, at 25°.

At the very low concentrations there is a third curve representing solutions in equilibrium with one of the solid solutions. There is a point of intersection of this curve and that along which dicalcium phosphate is the solid phase. At that point we should have present dicalcium phosphate, the solid solution of the limiting composition, liquid solution, and vapor, and with the temperature fixed there would be an invariant point. It will be seen from Table VIII that the composition of the limiting solid solution is quite close to that of dicalcium phosphate, but the analytical difficulties have made it impossible to determine the exact composition of the solid solution. The table shows, however, that the ratio $P_2O_5 : CaO$ in the limiting solid solution must be above 1.10 and below 1.27, and also that the composition of the liquid solution at that point lies between 0.40 and 0.54 gram CaO per liter and between 1.11 and 1.52 grams P_2O_5 per liter.

It has been demonstrated in the foregoing paragraphs that the term "solubility" as applied to the calcium phosphate in water has not the same meaning as when the term "solubility" is applied to such salts as calcium sulphate or sodium chloride. In the latter case the solution contains both acid and basic parts in the same ratio as they are present in the original solid, but in the case of a phosphate of calcium the addition of water causes an hydrolysis of the salt, the net result of which is to form a solution and a solid in which the ratio of acid to base is not the same. The composition of the solution and of the solid will depend not only on the temperature but also on the ratio of lime, phosphoric acid, and water in the mixture. Considerable experimental work has been done upon the effect of other salts upon the "solubility" of the calcium phosphates, and in every case it will be necessary to compare the solubility of the calcium phosphate in water with that in the salt solution.

The temperatures of certain invariant points have been announced quite recently by Bassett,[a] who has shown that at 30° another solid phase, anhydrous dicalcium phosphate, becomes stable and at that temperature five phases—the two forms of dicalcium phosphate (anhydrous and dihydrate), monocalcium phosphate, solution, and vapor—are in equilibrium. Another invariant condition is obtained at the highest temperature at which the dihydrate of dicalcium phosphate can exist in this three-component system. At about 80° there may be present the two forms of dicalcium phosphate (anhydrous and dihydrate), solid solution, liquid solution, and vapor. By heating the dihydrate of dicalcium phosphate with water, there is a change at the temperature 80°, the anhydrous salt appearing as one of the solid phases.

It is also announced that monocalcium phosphate may be obtained anhydrous by evaporating at 160° a solution containing phosphoric acid and lime, the ratio of acid (P_2O_5) to lime (CaO) being greater than 3. If this ratio be less than 3, the monohydrated salt is formed.

Discussion of Results.

From the above results it follows that monocalcium phosphate is decomposed by water, and that the nature of the decomposition products depends on the temperature and on the quantity of water employed. At low temperature and with moderate quantities of water, the solid which separates is the dihydrate of dicalcium phosphate, and at higher temperatures anhydrous dicalcium phosphate separates. In both cases the water holds in solution considerable quantities of phosphoric acid, together with as much of the solid as the acid solution can dissolve. When the ratio of water to salt is small, only a portion of the monocalcium phosphate reverts to dicalcium phosphate, and at any given temperature the resulting solution has a perfectly definite composition—for there are two solid phases, solution and vapor, and therefore no variance. When the ratio of water to salt originally mixed is very great, the decomposition of the solid goes even farther than dicalcium phosphate.

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[a] Chem. News, **95**, 21 (1907); Zeit. anorg. chem., **53**, 34 (1907).

These results may be stated in another way. At any definite temperature solid monocalcium phosphate exists in contact with solutions above a certain definite concentration. Solid dicalcium phosphate exists below that concentration down to a comparatively low one, below which even reverted phosphate suffers decomposition.

In the earlier experiments upon the "solubility" of monocalcium phosphate water was added to the solid until the solution became clear. The presence of considerable quantities of free phosphoric acid in the salt employed by these experimenters caused the wide deviations in the results.

It is apparent, too, that the usual method of determining the water-soluble phosphoric acid in fertilizers is open to the objection that practically all of the fertilizer is soluble if sufficient water be used. Moreover, the solubility of the most insoluble product obtained by leaching monocalcium phosphate is great enough to supply a growing crop. The present method for the determination of water-soluble phosphoric acid in fertilizers is open to the further objection that the quantity of phosphoric acid found in the leachings from the sample is dependent upon the quantity of water which has been added, upon the temperature, and upon the time of contact. It also depends on the manner of adding the water, whether in successive small portions or in fewer larger portions. The time factor is quite important, for it was shown that the equilibrium between a phosphate and water was attained only after a number of days had elapsed. Further, it will be shown that when phosphatic materials are treated with soil waters, which contain small quantities of mineral and organic materials, the fertilizers generally yield more phosphoric acid than they would to pure water.

From the above experiments, it would be expected that after a superphosphate is added to a soil, the concentration of phosphoric acid in the soil moisture would be very large. This state of affairs does exist in all probability for a short space of time, but this increase in concentration very rapidly diminishes again to the original concentration of the soil solution before the fertilizer was added. The work of Schreiner and Failyer[a] shows that soils to which phosphoric acid had been added, up to one-half of 1 per cent of the weight of the soil, furnished upon treatment with water a solution which was practically the same in composition as was the solution obtained in the same way before the phosphate was applied.[b] It follows, therefore, that fertilizers act essentially on the soil and indirectly on the plant, for the soil automatically reduces the concentration of the phosphate in the soil solution to the normal amount soon after any addition to the soil is made, which addition would otherwise tend to augment the concentration of the soil solution.[c] Furthermore, it is customary in many localities to fertilize some time before the crop is planted, and if by the time the crop is planted the soil solution has been reduced to the normal composition as regards the plant food constituents, it is evident that the action of the fertilizers must be upon the soil either to change its physical condition or else to react upon some materials which would have been harmful to the growing plant.

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[a] Bul. No. 32, Bureau of Soils, U. S. Dept. of Agr. (1906).

[b] The following conclusion is from a recent publication by Wheeler and Adams (Bul. No. 114, Rhode Island Expt. Sta. (1906), p. 137):

> If all soil solutions are of practically constant composition and of a strength sufficient to fully support plant growth and if they are continually maintained of the same strength, as seems to be held by the Bureau of Soils of the U. S. Department of Agriculture, it would be expected that these phosphates would not have acted so differently upon the different plants. The assumption that they acted as antitoxins and not in a manurial capacity, which is the explanation of the Bureau for many of the heretofore supposed manurial effects, is, in the light of to-day, too hypothetical to receive full credence, even though it has long been known that many ordinary constituents of fertilizers may act in rendering certain poisonous substances innocuous at the same time that they are fulfilling their manurial function.

It seems necessary to state again the position of the Bureau of Soils in this matter. This Bureau has never denied that the action of fertilizers may be to increase the store of plant food in the soil, and to supply a deficiency in the plant foods. The *chief* function of fertilizers, as has been affirmed on many occasions, is to react upon the soil, either to improve the physical condition or to render innocuous some substance or substances harmful to plants. It is surprising that "in the light of to-day" the interpretation of Wheeler and Adams should have been put upon the position of the Bureau of Soils.

[c] In a paper upon the determination of available plant food in soils, Hall and Amos [Jour. Chem. Soc., **89**, 205 (1906)], say:

> The results lend no support to Whitney's theory, that all soils will form in nature solutions of approximately constant composition, representing an equilibrium between the soil phosphoric acid and the solvent water which is independent of the mass of the former.

But they also say—and in the same paper—

> The concentration of the solution in equilibrium with the soil falls with each successive attack of the soil by the same solvent. This indicates the presence in the soil of several compounds of varying solubility, the mass of the more soluble being small and of the same order as the amounts going into solution in the earlier extracts. *When these more soluble compounds have been removed, an approximate constant equilibrium is attained between the phosphoric acid remaining in the soil and that going into solution at each extraction, indicating that after the more soluble compounds have been removed there remains a phosphate in each soil of such low solubility that the amount going into solution at each extraction is independent of the mass present in the soil.* [The italics are ours].

It is obvious that the authors have described the conditions obtaining in a soil. The attack of the soil by successive leachings of rain water ought, according to the theory advanced by these authors, to remove the more soluble phosphatic compounds and leave the phosphate of low solubility, which gives the constant soil solution as regards phosphoric acid. Far from lending "no support to Whitney's theory," these results offer exceedingly good confirmation of it.

ACTION OF SOLUTIONS ON THE PHOSPHATES OF CALCIUM.

Carbonic acid.

It has been shown by many authorities that water containing carbon dioxide in solution has a much greater solvent action on calcium phosphates than pure water. Dumas[a] observed that Seltzwater, which contains considerable quantities of carbon dioxide, etches ivory in a similar way to dilute solutions of hydrochloric acid. At 10° C. Lassaigne[b] observed that 100,000 parts of water saturated with carbon dioxide dissolve a small quantity of calcareous material from human bones. Liebig[c] found that one liter of water saturated with carbonic acid dissolves 0.6626 gram of bone phosphate, of which 0.500 separates out on boiling. The solvent action of carbon dioxide water was recorded by Warington,[d] who some years later[e] discovered that water had a decomposing action on so-called tricalcium phosphate. Dusart and Pelouze[f] showed that a gelatinous precipitate of calcium phosphate when treated with water saturated with carbon dioxide gave a solution in which boiling caused the precipitation of the phosphate and carbonate of lime. Thus the gelatinous phosphate of lime is more soluble in water carrying carbon dioxide than in pure water. The same experimenters have treated dicalcium phosphate with pure water and with water saturated with carbon dioxide. They found that the solubility in pure water is 0.28 parts per 1,000, while in water saturated with carbonic acid it is 0.66 part in 1,000. The action of carbonated water upon various natural phosphates as determined by Williams[g] is given in Table IX.

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[a] Compt. rend., **23**, 1018 (1846).

[b] Compt. rend., **23**, 1019 (1846).

[c] Ann. Chem. Phar., **61**, 128 (1847).

[d] Jour. Chem. Soc., **19**, 296 (1866); **24**, 80 (1871).

[e] Jour. Chem. Soc., **26**, 983 (1873).

[f] Compt. rend., **66**, 1327 (1868).

[g] Chem. News, **24**, 306 (1871); Jour. Chem. Soc., **25**, 269 (1872).

TABLE IX.—*The solubility in water of various phosphatic materials used as fertilizers.*

Source of phosphate.	Water required to dissolve one part of the phosphate.
	Parts.
Apatite from Perth, Canada, containing 89.27 per cent $Ca_3(PO_4)_2$	222,000
Same, levigated	140,000
Finely ground bone containing 56.78 per cent $Ca_3(PO_4)_2$	5,698
Same, calcined to burn out organic matter, 92.88 per cent $Ca_3(PO_4)_2$	8,029
Adulterated commercial bone dust containing 24.32 per cent organic and volatile matters and 35 per cent $Ca_3(PO_4)_2$	4,122
South Carolina phosphate containing 57.89 per cent $Ca_3(PO_4)_2$	6,983
Same, levigated	6,544
Guano containing 49.67 per cent $Ca_3(PO_4)_2$	8,009

Maly and Donath[a] have shown that carbonated water increases the apparent solubility of bone phosphate. Similar results have been obtained by Joffre[b] on the comparative solubility of calcium phosphate in pure water and in water carrying carbon dioxide. The solubility of tricalcium phosphate in pure water was found to be 0.009 gram $Ca_3(PO_4)_2$ per liter, and in water saturated with carbon dioxide 0.153 gram, and in another experiment 0.161 gram $Ca_3(PO_4)_2$ per liter. The solubility of powdered apatite was found to be augmented by the presence in solution of carbonic acid gas. Pure water dissolved 0.002 gram $Ca_3(PO_4)_2.1/3CaF_2$ per liter, while water saturated with carbon dioxide dissolved 0.014 gram of the apatite. As superphosphates form a basic calcium phosphate when applied to a soil, which gelatinous precipitate is more soluble both in pure water and in water carrying carbon dioxide than is apatite, Joffre concludes that this fact accounts for the different action of the two forms of phosphate and he states that there is much in favor of the use of superphosphates.

More detailed experiments have been published by Schloesing,[c] who has treated one gram of a phosphate of lime, whose analysis was very close to $Ca_3(PO_4)_2.H_2O$, with 1,250 c.c. of various solvents at 16° to 20° for one day. The following table shows the results:

TABLE X.—*Solubility of lime phosphate in water containing carbon dioxide and calcium carbonate.*

Solvent.	P_2O_5 per liter.	CaO per liter.
	Mg.	*Mg.*
Water	0.74	
1,200 c.c. distilled water and 50 c.c. water saturated with CO_2	6.9	
1,000 c.c. distilled water and 250 c.c. water saturated with CO_2	48.5	
1,250 c.c. water saturated with CO_2	91.9	
Water containing 174 mg. $CaCO_3$ and 82 mg. CO_2 per liter	.38	100.0
Water containing 290 mg. $CaCO_3$ and 171 mg. CO_2 per liter	1.1	162.3
Water containing 389 mg. $CaCO_3$ and 270 mg. CO_2 per liter	.80	218.8
Water containing 488 mg. $CaCO_3$ and 415 mg. CO_2 per liter	1.77	273.3
Water containing 558 mg. $CaCO_3$ and 541 mg. CO_2 per liter	1.30	312.7

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[a] Jour. prakt. Chem., **115**, 413 (1873).

[b] Bul. Soc. Chim. (3), **19**, 372 (1898).

[c] Compt. rend., **131**, 149 (1900).

The above table indicates that tricalcium phosphate shows an increasing solubility in water containing increasing quantities of carbon dioxide, and that the solubility of tricalcium phosphate in pure water and in carbonated waters saturated with carbonate of lime is very slight, being about one or two parts per million of solution. In a later paper by Schloesing[a] this has been confirmed, for a phosphate solution added to a solution of calcium bicarbonate was found to precipitate tricalcium phosphate. The solubility of dicalcium phosphate is also augmented by the presence of carbonic acid in solution.

TABLE XI.—*Solubility of lime phosphate in water containing carbon dioxide.*

Solvent.	CaO per liter.	P_2O_5 per liter.
	Mg.	*Mg.*
Boiled water	39.4	49.8
Water containing 0.81 gram CO_2 per liter	77.9	100.7
Water saturated with CO_2	173.7	346.8

Cameron and Seidell[b] have determined the solvent action of carbon dioxide on the phosphates of calcium in solutions saturated with gypsum and calcium carbonate.

TABLE XII.—*Action of water and solutions upon tricalcium phosphate.*

[Time of contact 35 days. T=25° C.]

$Ca_3(PO_4)_2$ per liter.	Without CO_2.		With CO_2.	
	Ca per liter.	PO_4 per liter.	Ca per liter.	PO_4 per liter.
Grams.	*Gram.*	*Gram.*	*Gram.*	*Gram.*
5	0.0142	0.109	0.085	0.239
10	.019	.189	.114	.344
20	.031	.324	.114	.481
40	.050	.558	.134	.738
IN CONTACT WITH SOLID CALCIUM SULPHATE.				
5	0.620	0.113	0.646	0.217
10	.640	.205	.659	.315
20	.644	.360	.662	.451
40	.666	.623	.682	.715
IN CONTACT WITH SOLID CALCIUM CARBONATE.				
5	0.034	Trace.	0.352	Trace.
10	.073	Trace.	.354	Trace.
20	.106	Trace.	.327	Trace.
40	.134	Trace.	.306	Trace.

[a] Compt. rend., **131**, 211 (1900).

[b] Jour. Am. Chem. Soc., **26**, 1454 (1904).

TABLE XIII.—*Action of water and solutions upon dicalcium phosphate.*

[Time of contact 38 days. T=25° C.]

$CaHPO_4$ per liter.	Without CO_2.		With CO_2.	
	Ca per liter.	PO_4 per liter.	Ca per liter.	PO_4 per liter.
Grams.	*Gram.*	*Gram.*	*Gram.*	*Gram.*
5	0.039	0.090	0.169	0.392
10	.033	.116	.160	.388
20	.036	.117	.162	.395
40	.039	.131	.166	.402
IN CONTACT WITH SOLID CALCIUM SULPHATE.				
5	0.619	0.016	0.683	0.299
10	.624	.016	.690	.306
20	.622	.040	.687	.281
40	.636	.064	.687	.299
IN CONTACT WITH SOLID CALCIUM CARBONATE.				
5	0.110	0.037	0.291	0.084
10	.110	.043	.284	.089
20	.119	.043	.289	.080
40	.120	.045	.313	.081

These tables show that both aqueous and carbonic acid solutions saturated with calcium carbonate dissolve much less of the phosphates of calcium than the same solutions free of calcium carbonate. Saturated solutions of calcium sulphate, with carbon dioxide, dissolve slightly more tricalcium phosphate than the solution without gypsum. In the presence of carbon dioxide, however, the quantity dissolved is slightly less. Somewhat more dicalcium phosphate is dissolved by water and by water carrying carbon dioxide than by the same solvents saturated with gypsum.

Sulphurous acid.

Suspensions of various samples of the phosphates of calcium are cleared up by passing sulphur dioxide into the suspension. In a large number of experiments Gerland[a] has shown that pure calcium phosphate and commercial bone ash are quite soluble in sulphur dioxide solution, the solubility being greater in solutions richer in sulphur dioxide. Upon allowing these solutions to stand, upon heating, or upon addition of alcohol, a precipitate formed which was of variable composition. When the residual solution still contained moderate quantities of sulphur dioxide the precipitate was shown to be either pure dicalcium phosphate or dicalcium phosphate with calcium sulphate. In the latter cases a microscopical examination of the precipitate showed that it was composed of two crystal species. Upon evaporation of the solutions until very little sulphur dioxide remained in solution, a precipitate was obtained corresponding very closely to $Ca_3(PO_4)_2.SO_2+2H_2O$. It is claimed that this substance is not a mixture of dicalcium phosphate and calcium sulphite, for it does not behave like an ordinary sulphite, as it is quite stable in the presence of oxidizing agents, like chlorine. According to later experiments of Rotondi,[a] this precipitate is a mixture of dicalcium phosphate and calcium sulphite.

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[a] Jour. prakt. Chem., **112**, 97 (1871).

The action of sulphurous acid solutions upon the phosphates of calcium resembles that of other acids. In the concentrated acid solutions the stable solid phosphate is the monocalcium phosphate; in less concentrated solutions the stable solid is dicalcium phosphate, while in the dilute solutions a more basic phosphate separates, which according to Gerland is an addition product of tricalcium phosphate and sulphurous acid.

Citrate solutions.

The solvent action of various citrate solutions upon tricalcium phosphate has been investigated by Erlenmeyer.[b] The solutions employed were (1) a solution of crystalline diammonium citrate of density 1.09; (2) a solution of triammonium citrate of the same density; (3) a one-fourth per cent citric acid solution (Tollens solution). To solutions 1 and 2 one per cent of the phosphate was added and the solution kept at 35°–38° C., while one-fourth per cent of phosphate was added to the third solution.

Table XIV.—*Action of various citrate solutions on calcium phosphate.*

Calcium phosphate.	Per cent of original P_2O_5 dissolved.		
	In acid citrate solution.	Neutral citrate solution.	Citric acid solution.
	Per cent.	*Per cent.*	*Per cent.*
Air-dry $Ca_3(PO_4)_2+11H_2O$	100	55.06, 55.80	83.89, 83.79
Dried at 50°, $8Ca_3(PO_4)_2+15H_2O$	100	52.27, 52.34	....
Ignited, $Ca_3(PO_4)_2$	93.55, 92.91	31.85, 31.99	53.33, 53.39

Terreil[c] has also studied the effect of citric acid solution upon tricalcium phosphate. A saturated solution of the phosphate in the acid solution was just neutralized with ammonia or potash. The clear solution was then analyzed for lime and phosphoric acid. In these experiments the dilutions are not given. Every 100 grams of citric acid neutralized with ammonia dissolved 6.95 and 7.08 grams of the phosphate and, when neutralized with potash, 2.02 and 1.78 grams of the phosphate. From these experiments the conclusion is drawn that ammonium citrate solutions have a greater solvent action on the basic phosphate of lime than have potassium or sodium citrate solutions.

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[a] Annali di Chimica, **74**, 129 (1882); abstr. in Ber., **15**, 1441 (1882).

[b] Ber., **14**, 1253 (1881).

[c] Bul. Soc. Chim. (2), **35**, 548 (1881).

Ammonium compounds.

Many authors[a] have recorded the remarkable solvent effect of ammonium compounds upon the basic phosphate of lime. The results of Terreil indicate the relative solvent action of various ammonium salts upon tricalcium phosphate. In each case 100 grams of the acid were neutralized with ammonia, and the following quantities of the phosphate were dissolved: Hydrochloric acid, 0.650 and 0.660 gram; nitric acid, 0.309 gram; sulphuric acid, 1.050 grams; acetic acid, 0.255 gram; tartaric acid, 4.59 and 4.53 grams; citric acid, 6.95 and 7.08 grams; malic acid, 1.07 and 1.18 grams of tricalcium phosphate.

Dry ammonia gas has been shown by Bassett[b] to have no action upon either the dihydrate of dicalcium phosphate or anhydrous dicalcium phosphate at ordinary temperature. Above 80°, however, the dihydrate gives off water which decomposes the salt partially. This solution absorbs ammonia gas vigorously, and solids are formed which, according to Bassett, are tricalcium phosphate and diammonium phosphate.

Monocalcium phosphate reacts with dry ammonia gas very slowly at the ordinary temperature, but the reaction is rapid at 100° C. The double compound $Ca(NH_4)_2H_2(PO_4)_2$ is first formed, which is not stable in the presence of the water formed in the reaction. The decomposition products are diammonium phosphate and dicalcium phosphate dihydrate, the reaction coming to an end when sufficient dicalcium phosphate dihydrate is formed to absorb all the water. When water and ammonia are added in excess, the final products, according to Bassett, are diammonium phosphate and tricalcium phosphate.

Calcium salts.

The effect of calcium carbonate in carbonic acid solutions has already been shown[c] to depress the solubility of calcium phosphate. In the following tables[d] are given the results with solutions of calcium chloride, calcium chloride and hydrochloric acid, and of calcium nitrate, from which it appears that increasing the concentration with respect to the lime salt decreases the amount of phosphoric acid entering the solution. This effect may possibly be ascribed to the formation of a common ion (Ca) from both substances and a "forcing back" of the solubility of the calcium phosphate and in consequence a lessening of the amount of phosphoric acid entering the solution.

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[a] Dumas, Compt. rend., **23**, 1018 (1846); Liebig, Ann. Chem. Phar., **61**, 128 (1847); **106**, 185 (1858); Warington, Jour. Chem. Soc., **19**, 296 (1866); Maly and Donath, Jour. prakt. Chem., **115**, 413 (1873); Terreil, Bul. Soc. Chim. (2), **35**, 548 (1881), et al.

[b] Chem. News, **95**, 21 (1907); Zeit. anorg. Chem., **53**, 49 (1907).

[c] See page 27.

[d] Cameron and Hurst, Jour. Am. Chem. Soc., **26**, 908 (1904).

TABLE XV.—*Tricalcium phosphate in solutions of calcium chloride when in the proportion of 1 gram of calcium phosphate to 40 c.c. solution.*

[Temperature, 25° C. Time, 5 days, with continuous shaking and one day settling.]

$CaCl_2$ per liter.	PO_4 per liter.	$CaCl_2$ per liter.	PO_4 per liter.
Grams.	*Gram.*	*Grams.*	*Gram.*
0	0.2185	25	0.0979
1	.1383	50	.0905
5	.1150	100	.0797
10	.1050	200	.0626

TABLE XVI.—*Tricalcium phosphate in solution of calcium chloride when in the proportion of 1 gram calcium phosphate to 100 c.c. solution.*

[Temperature, 25° C. Time, 15 days, with frequent shaking.]

$CaCl_2$ per liter.	PO_4 per liter.	$CaCl_2$ per liter.	PO_4 per liter.
Grams.	*Gram.*	*Grams.*	*Gram.*
2.5	0.0684	12.5	0.0548
5.0	.0604	25.0	.0511
6.25	.0600	50.0	.0502

TABLE XVII.—*Calcium phosphate in N/200 hydrochloric acid containing calcium chloride in the proportion of 1 gram calcium phosphate to 40 c.c. solution.*

[Temperature, 25° C. Time, 5 days, with continuous shaking and one day settling.]

$CaCl_2$ per liter.	PO_4 per liter.	$CaCl_2$ per liter.	PO_4 per liter.
Grams.	*Gram.*	*Grams.*	*Gram.*
0	0.3154	25	0.2254
1	.2745	50	.2125
5	.2527	100	.1878
10	.2455	200	.1421

TABLE XVIII.—*Calcium phosphate in solutions of calcium nitrate, when in the proportion of 1 gram calcium phosphate to 40 c.c. solution.*

[Temperature, 25° C. Time, 16 days, with constant shaking.]

$CaCl_2$ per liter.	PO_4 per liter.	$CaCl_2$ per liter.	PO_4 per liter.
Grams.	*Gram.*	*Grams.*	*Gram.*
0	0.2163	25	0.1064
1	.1907	50	.1098
5	.1110	100	.1132
10	.1053	200	.1093

TABLE XIX.—*Calcium phosphate in solution of calcium nitrate when in proportion of 1 gram calcium phosphate to 100 c.c. solution.*

[Temperature, 25° C. Time, 16 days, with constant shaking.]

$CaCl_2$ per liter.	PO_4 per liter.	$CaCl_2$ per liter.	PO_4 per liter.
Grams.	*Gram.*	*Grams.*	*Gram.*
2.5	0.0598	12.50	0.0223
5	.0452	25	.0045
6.25	.0404	50	Trace.

Potassium chloride.

It might be expected that potassium chloride, having no ion in common with calcium phosphate, would increase its solubility. From the results of Cameron and Hurst[a] given in the following table, there is shown to be a decomposing as well as a solvent action; with increasing concentration of the solution with respect to potassium chloride the calcium phosphate yields a decreasing amount of phosphoric acid and an increasing amount of the base.

TABLE XX.—*Tricalcium phosphate in solutions of potassium chloride.*

[Temperature, 25° C. Time, 30 days, with frequent shaking.]

1 gram $Ca_3(PO_4)_2$ in solution.	KCl per liter.	PO_4 per liter.	Ca per liter.
	Grams.	*Gram.*	*Gram.*
20 cubic centimeters	5	0.3278	0.0357
	25	.3227	.0829
	75	.3193	.1129
	150	.2971	.1286
	300	.2356	.1329
40 cubic centimeters	5	.2265	.0329
	25	.2224	.0614
	75	.2157	.0672
	150	.2151	.0757
	300	.2137	.0800
100 cubic centimeters	5	.1280	.0286
	25	.1273	.0329
	75	.1240	.0457
	150	.1126	.0400
	300	.1032	.0415

Sodium nitrate.

Liebig[b] has shown that sodium nitrate has an appreciable solvent action on the phosphates of calcium, for in a liter of solution containing 3 grams of the nitrate 0.079 gram dicalcium phosphate was dissolved. In another liter of solution 0.033 gram of tricalcium phosphate was dissolved. The results of Cameron and Hurst[c] given in the following table indicate that sodium nitrate has also a decomposing action on calcium phosphate.

TABLE XXI.—*Tricalcium phosphate in solutions of sodium nitrate.*

[Temperature, 25° C. Time, 30 days, with frequent shaking.]

1 gram $Ca_3(PO_4)_2$ in solution.	$NaNO_3$ per liter.	PO_4 per liter.	Ca per liter.
	Grams.	*Gram.*	*Gram.*
20 cubic centimeters	5	0.3073	0.0643
	25	.2971	.1572
	75	.3244	.1978
	150	.3142	.3901
	300	.3190	.5916
40 cubic centimeters	5	.1889	.0329
	25	.2291	.0757
	75	.2372	.1057
	150	.2425	.1343
	300	.2077	.1315
100 cubic centimeters	5	.1313	.0272
	25	.1300	.0486
	75	.1313	.0600
	150	.1304	.0729
	300	.1404	.0843

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[a] Jour. Am. Chem. Soc., **24**, 885 (1904).

[b] Ann. Chem. Phar., **106**, 185 (1858).

[c] Jour. Am. Chem. Soc., **24**, 885 (1904).

Sodium chloride.

That sodium chloride dissolves calcium phosphate present in the soil is shown in papers by Liebig,[a] Lassaigne,[b] Mandl,[c] and Maly and Donath.[d]

Other solvents.

Mandl[e] has stated that the phosphate of lime is soluble to a remarkable extent in gelatine, sugar, and albumen; and Bobierre[f] has shown that calcium phosphate found in the residues of sugar refining is held in solution by calcium sucrate.

SUPERPHOSPHATES.

On page 22 of this bulletin there are given the results of investigations on the three-component system—lime, phosphoric acid, water. It was found that there are three solubility curves, one representing solutions in equilibrium with monocalcium phosphate ($CaH_4(PO_4)_2.H_2O$), one representing solutions in equilibrium with dicalcium phosphate ($CaHPO_4.2H_2O$), and the third representing solutions in equilibrium with a series of solid solutions. The compositions of these solid solutions extend from pure lime to a solid of nearly the same composition as dicalcium phosphate. Another three-component system—lime, sulphuric acid, water—has been studied in this laboratory.[g]

The composition of solutions which are acid—i. e., those in which sulphuric acid is in excess of lime—has been published in the first paper, while the composition of solutions which are alkaline has been investigated in the second paper. Only one solid phase was found in this first investigation, viz, gypsum ($CaSO_4.2H_2O$). Had the investigation extended to more concentrated solutions of sulphuric acid, another solid phase, anhydrite ($CaSO_4$), would undoubtedly have been found. In the case of the alkaline solutions, two solid phases were found, calcium hydroxide and gypsum. In solutions containing less than 1.22 grams of free lime per liter the solid phase was found to be calcium hydroxide.

The following paragraphs will deal with the four-component system—lime, phosphoric acid, sulphuric acid, water, the essential constituents of the so-called "superphosphates."

The quantities of lime and phosphoric acid in solution when sulphuric acid is added to tricalcium phosphate have been given by

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[a] Ann. Chem., Phar., **61**, 178 (1847); **106**, 185 (1858).

[b] Jour. Chim. méd. (3), **3**, 11 (1847).

[c] Compt. rend., **44**, 1108 (1857).

[d] Jour. prakt. Chem., **115**, 413 (1873).

[e] Compt. rend., **44**, 1108 (1857).

[f] Compt. rend., **32**, 859 (1851).

[g] Cameron and Breazeale, Jour. Phys. Chem., **7**, 571 (1903); Cameron and Bell, Jour. Am. Chem. Soc., **28**, 1220 (1906); Bul. No. 33, Bureau of Soils, U. S. Dept. Agr. (1906), p. 47.

Armsby,[a] but no concentrations are given and the results will not, therefore be quoted.

A complete representation of the conditions obtaining in any four-component system can be attained only by the use of a space model. Such a space model for this four-component system would have as axes the amounts of lime, sulphuric anhydride, and phosphoric anhydride per liter of solution. With the densities known, the amount of water in these solutions can be computed. However, this representation is cumbrous and so we have represented the results on one of the projections of this space model, viz, on the coordinate plane bounded by the SO_3–axis and by the P_2O_5–axis. In other words, we have used a plane diagram representing all the conditions, with the exception of the lime content of the solutions. These conditions are described in the accompanying diagram (fig. 3), in which some of the fields are so narrow as to necessitate their distortion in order to show plainly the regions involved.

In figure 3, I, O represents a saturated solution of lime in water. On the OX axis, A represents the solution in equilibrium with dicalcium phosphate and the limiting solid solution; B represents the solution saturated with respect to both dicalcium phosphate and monocalcium phosphate. On the other axis, C represents the solution saturated with both calcium hydroxide and gypsum, and D the solution in equilibrium with both gypsum and anhydrite. The positions of the points A, B, C have been found by direct experiment, while the position of the point D has been determined in an indirect way. This method was adopted, since the change of gypsum to anhydrite, or vice versa, has been shown to be very slow. In their work on the various forms of calcium sulphate, van't Hoff[b] and Weigert have shown that at vapor pressures lower than 17.5 mm. at 25° C., gypsum is transformed to natural anhydrite, and above that pressure the reverse change takes place. Applying this result to the present problem, we have determined the strength of sulphuric acid which has a vapor pressure of 17.5 mm. when saturated with gypsum. The sulphuric acid solution having this vapor pressure has been found, from the results of Richards,[c] to have a density of 1.235. This solution contains 25.71 per cent SO_3,[d] or 317.5 grams SO_4 per liter. In this consideration no correction is made for the effect of the calcium sulphate in solution on the vapor pressure, a correction which would be very small because of the low solubility of gypsum in sulphuric acid of that strength. This solubility has been estimated by extrapolation from the results of Cameron and Breazeale[a] to be approximately 1 gram of calcium sulphate per liter of solution.

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[a] Jour. prakt. Chem., **121**, 333 (1876).

[b] Sitzungsber. Akad. Wiss. Berlin, 1901, 1140.

[c] Proc. Am. Acad., **33**, 23 (1897–98).

[d] Fresenius "Qualitative Analysis," 1899, p. 676.

The determination of the possible fields has been investigated by adding small quantities of sulphuric acid to various solutions represented on the diagram by points on the line OX. In all cases the addition of a little sulphuric acid causes a white precipitate, which upon microscopic analysis proved to be gypsum. This indicates that the fields over which the phosphates of calcium can exist are very narrow indeed. An analysis for sulphates was made of three of these

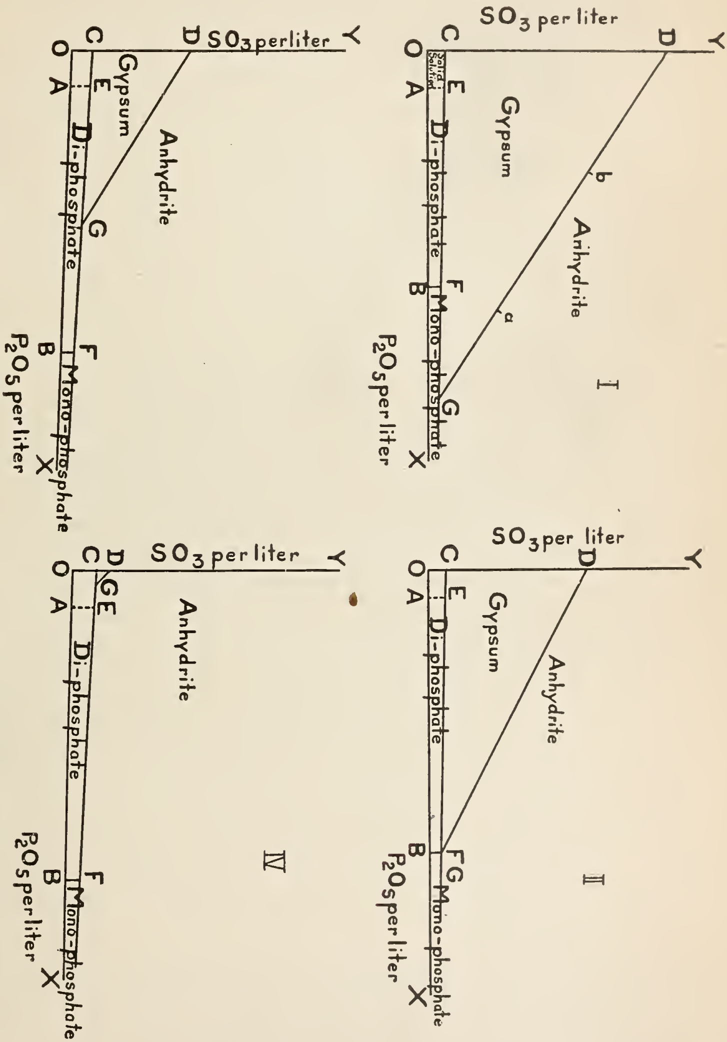

Fig. 3.—Diagrams showing the composition of solutions in contact with the components of superphosphate at various temperatures.

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[a] Loc. cit.

solutions, one about midway between A and B in the diagram, one very near B, and the third on BX. The sulphuric acid content of these three solutions was found to be 0.9, 0.6, and 0.3 gram SO_4 per liter, respectively, and hence the line CEFG lies very close to OX, the two lines converging as we pass to the right. Analyses of some of these solutions have been made by Cameron and Seidell,[a] their lime content and phosphoric acid content being practically the same when no gypsum is present as it is when the solution is saturated with respect to gypsum. These solutions lie on the line EF, near the point E. Thus it is evident that the presence of gypsum has no appreciable effect on either the lime content or the phosphoric acid content of the solutions, and as the amount of sulphate in solution is greater in this region than it is farther to the right, it is apparent that the solutions near F and to the right of F have the same lime content and phosphoric acid content as those on the axis OX. The positions of the points E and F have therefore been taken as almost identical with the positions of A and B.

Finally, the position of the line forming the boundary between the gypsum and anhydrite fields has been found. From the work of van't Hoff and Weigert, which has been cited above, the vapor pressure at which gypsum and anhydrite remain in equilibrium at 25° C. is 17.5 mm. Consequently the solutions on the diagram which have that vapor pressure are on the boundary line between the two fields. In these determinations we have not attempted to obtain equilibrium conditions, but we have found whether various solutions had vapor pressures above or below this value. This has been accomplished by placing a weighed solution (25 grams of solution in a weighing bottle) known to have this vapor pressure in a bottle containing the unknown solution. After a time the former solution was again weighed, and from the loss or gain it has been found whether the vapor pressure of the unknown solution was above or below 17.5 mm. In this way the position of the point G has been determined, at which point gypsum, anhydrite, and monocalcium phosphate coexist as solids in equilibrium with a solution. Also we have found the position of two points, *a* and *b*, along the line DG which separates the gypsum field from the anhydrite field.

To determine the point G various solutions along BX, whose vapor pressures are not different from those along FG, have been investigated with the following results: The solution containing 485 grams P_2O_5 per liter caused an increase in weight of 0.080 gram in two days; the solution containing 563 grams P_2O_5 per liter caused a decrease in weight of 0.026 gram in two days. As these experiments were carried on under identical conditions we have interpolated to find that solution which should show no change in weight. This has been found to contain 545 grams P_2O_5 per liter, and therefore G is determined. The positions of the points *a* and *b* have been found by similar pairs of determinations. The composition of the solution at *a* is 350 grams P_2O_5 per liter and 120 grams SO_3 per liter, and the composition at *b* is 150 grams P_2O_5 per liter and 275 grams SO_3 per liter.

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[a] Jour. Am. Chem. Soc., **26**, 1461 (1904).

TABLE XXII.—*Data for the constant solutions at 25° C.*

Point.	P_2O_5 per liter.	SO_3 per liter.	CaO per liter.	Solid phases present.
	Grams.	*Grams.*	*Grams.*	
O	0	0	1.17	$Ca(OH)_2$.
A	3	0	1.5	Solid solution; $CaHPO_4.2H_2O$.
B	317	0	77	$CaH_4(PO_4)_2.H_2O$; $CaHPO_4.2H_2O$.
C	0	0.9	1.9	$Ca(OH)_2$; $CaSO_4.2H_2O$.
D	0	317.5	1	$CaSO_4.2H_2O$; $CaSO_4$.
E	3	0.9	1.5	Solid solution; $CaSO_4.2H_2O$; $CaHPO_4.2H_2O$.
F	317	0.6	77	$CaSO_4.2H_2O$; $CaHPO_4.2H_2O$; $CaH_4(PO_4)_2.H_2O$.
G	545	0.2	38	$CaSO_4.2H_2O$; $CaSO_4$; $CaH_4(PO_4)_2.H_2O$.

To describe the conditions which obtain at any other temperature than 25° C. it is necessary to determine how the various points on the diagram are affected by changes of temperature, and also to determine whether any new solid phases appear. In the present case a microscopic examination of the crystals formed at the higher temperature has revealed no new types and it is therefore probable that there are no new solid phases. Above the temperature 66° the solid gypsum, stable at all lower temperatures, becomes unstable and therefore does not appear on the diagram representing the conditions at 66°. It has been found by experiment that the points B and F move to the right with rising temperature. In other words the two phosphates of calcium coexist in solutions which become richer in phosphoric acid as the temperature increases. The points E and A have not been investigated at any temperature other than 25° C., but it is certain from qualitative experiments that at higher temperatures there is a field for solid solutions just as there is at 25°. This has been indicated by the dotted line EA. The direction in which the point D moves with change of temperature can be predicted from the results of van't Hoff and Weigert[a] upon the vapor pressure at which gypsum and anhydrite exist in equilibrium.

The composition of sulphuric acid solutions which have the same vapor pressure at 10°, 25°, and 35° has been computed from the data upon the vapor pressures of these solutions,[b] with the following results. It is apparent that the point D approaches C with rise of temperature.

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[a] Loc. cit.

[b] Landolt and Börnstein, Phys.-Chem. Tabellen (1905), pp. 166–167.

TABLE XXIII.—*Vapor pressures at which gypsum and anhydrite coexist at various temperatures, and composition of sulphuric acid solutions with the same vapor pressure.*

Temperature.	Vapor pressure at which gypsum and anhydrite coexist.	Composition of H_2SO_4 solutions with same vapor pressures in per cent H_2SO_4.
° *C.*	*mm.*	*Per cent.*
10	5.79	37.6
25	17.5	31.5
35	32.2	28.5
66	150	0

At 66° gypsum and anhydrite coexist in contact with their own solution in water. The presence of lime, whose solubility in water at this temperature is less than 1 gram per liter, will lower this temperature very slightly. Similarly along the line C E G F, the point G is continually moving toward the point C. Consequently it is evident that the field for gypsum disappears at a temperature of 66° and anhydrite becomes the stable solid over a great range of solutions.

It is evident that at some temperature intermediate between 25° and 66° the point F, which is moving to the right with increasing temperature, will meet the point G, which is moving to the left. At this point we have a sextuple point, or six phases—vapor, solution, and the four solids, anhydrite, gypsum, monocalcium, and dicalcium phosphates. This state of affairs can exist at only one temperature and one vapor pressure. This is shown diagrammatically in figure 3, II. As the temperature increases still further, the points D and G approach C, and figure 3, III, illustrates the state of affairs at some temperature below 66°. At the temperature 66° the field for gypsum disappears altogether.

From the preceding results and diagram the effects of water upon a mixture of the salts may be deduced. The following considerations will disregard the effect of substances other than gypsum and monocalcium phosphate, which substances are nearly always present in commercial superphosphates, viz, ferric phosphate, aluminum phosphate, calcium chloride, or fluoride, etc. All these substances will have some influence upon the positions of the various points and lines in the above diagram, but if their amount be small their influence may be neglected. Suppose a superphosphate composed of gypsum and monocalcium phosphate be leached at 25° C. The addition of water to monocalcium phosphate crystals causes a partial change to dicalcium phosphate and a solution saturated with respect to both phosphates. A small amount of gypsum will also pass into the solution. If water be added to this solution, or if the solution be drained away and fresh water added, more of the monocalcium phosphate will disappear and dicalcium phosphate will be formed. The net effect of this leaching is to wash out some free phosphoric acid, together with considerable quantities of calcium and a very small quantity of gypsum. If the addition of water is rapid, the time for this change may be very short indeed. During this change the composition of the solution is represented by the point F of figure 3, and if equilibrium conditions are obtained the composition of the solution will remain constant until *all* the monocalcium phosphate disappears. It will be observed that the greater part of the original calcium phosphate has been removed. This may be partially represented by the equation

$$CaH_4(PO_4)_2 = CaHPO_4 + H_3PO_4,$$

all the phosphoric acid in excess of the compound $CaHPO_4$ being leached away, together with a considerable amount of the diphosphate, which is dissolved. Upon the removal of some of the solution and the dilution of the residue by fresh water, the composition of the leachings will change rapidly until the point E is reached. Here another change takes place, the crystalline dicalcium phosphate giving up phosphoric acid, which carries some of the phosphate into solution. The solid changes to a solid solution of lime and phosphoric acid, and upon continued leaching this solid solution changes gradually to that solid solution which in saturated gypsum solutions dissolves unchanged, i. e., the ratio of lime and phosphoric acid which have gone into solution is the same as in the solid solution. Over this range of concentrations gypsum has a much higher solubility and it will probably disappear before the solid solutions have all disappeared.

The process of leaching of superphosphate may therefore be divided conveniently into four stages: First, monocalcium phosphate disappears and solid dicalcium phosphate and a solution of phosphoric acid containing much of the lime are formed. The weight of the resulting dicalcium phosphate is less than one-half of the original monocalcium phosphate. Very little gypsum has gone into solution at this stage. The second stage consists in the complete change of dicalcium phosphate into an amorphous solid solution, and very much more gypsum goes into solution. The third stage in the leaching process is the gradual change in the solid solution to one containing relatively less phosphoric acid and more lime. The liquid solutions are now quite dilute, and consequently gypsum will dissolve freely, and it is certain that the gypsum will all be washed away before the calcium phosphate (as solid solution) has been all dissolved. The fourth stage consists in the slow solution in water of a relatively insoluble solid solution of lime in phosphoric acid, which contains relatively more lime than would be required by the formula $Ca_3(PO_4)_2$.

When superphosphates are allowed to stand for some time or when they are applied to the soil they more or less rapidly go through a process known as "reversion," with the result that the phosphoric acid becomes much less soluble. According to some authors "reverted" phosphate is essentially dicalcium phosphate. This reversion has been variously ascribed to the presence of tricalcium phosphate, to iron and alumina, and to various recondite and unknown causes. According to Wiley[a] "the expression 'reverted phosphoric acid,' therefore, in practice not only includes a dicalcium phosphate, which once may have been the monocalcium salt, but also all of that salt originally existing in the superphosphate, and formed regularly during its manufacture, as well as any iron and aluminum phosphates present which are soluble in ammonium citrate. The expression 'citrate soluble' is therefore to be preferred to 'reverted' phosphoric acid."

Investigations of the process of "reversion" have generally been based on the supposed distinction of the solubility of dicalcium phosphate and insolubility of tricalcium phosphate in solutions of ammonium citrate. As a matter of fact, however, the ammonium citrate solution ordinarily employed dissolves considerable quantities of phosphoric acid and at the same time lesser quantities of lime, forming a substance which has the composition indicated by the formula $Ca_3(PO_4)_2$, or one which is even richer in lime. In this laboratory Mr. W. O. Robinson has found that when a sample of precipitated calcium phosphate of a composition approximating $Ca_3(PO_4)_2$ was treated with solutions of ammonium citrate large quantities of both phosphoric acid and lime were obtained in solution. But it was also found that the apparent solubility of the phosphate was dependent upon the proportion of solid to solvent employed. In the manufacture of superphosphate by mixing sulphuric acid with finely ground phosphatic material, it is customary to add an amount of acid somewhat short of that required by theoretical considerations to change completely all the material to a monophosphate. Moreover, at the end of the mixing process it is certain that equilibrium conditions have not been realized, for experiments have shown that if a sample of the material be inclosed in a sealed container for some months the water-soluble phosphoric acid becomes less. When the acidulated mass is removed from the mixing tanks it yet contains some of the original phosphatic material unacted on. When piled in the drying sheds the reaction continues, induced in part by the absorption of moisture from the air. One of these reactions is between the monophosphate and the undecomposed phosphate remaining, with the formation of dicalcium phosphate. But owing to the relatively large amount of water required for the formation of the dicalcium salt ($CaHPO_4.2H_2O$) the rate of reaction is slow, depending upon the gradual absorption of moisture from the air. When, however, the superphosphate is added to the soil, reversion is unquestionably very rapid, owing to the relatively large amount of water available and the large amount of basic material which can and does absorb the liberated acid.

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[a] Principles and Practices of Agricultural Analysis, vol. 2, p. 140, 1895.

From the facts brought out above it is apparent not only that the usual method of determining the citrate-soluble phosphoric acid does not determine the sum of the dicalcium, iron, and aluminum phosphates, but also that the more basic lime phosphates are decomposed by the citrate solution and yield some of their phosphoric acid and lime to the solution. There seems to be no good reason therefore why this solution should be used as a basis for the commercial valuation of phosphatic fertilizers, rather than other solutions, except that this solution decomposes the phosphates much more readily than most others. When applied to a soil, however, the decomposition of a phosphatic fertilizer is brought about by water carrying, as a rule, very minute quantities of mineral and organic material, and there seems to be no obvious parallel between the citrate-soluble phosphoric acid and that which immediately or ultimately passes into the soil solution.

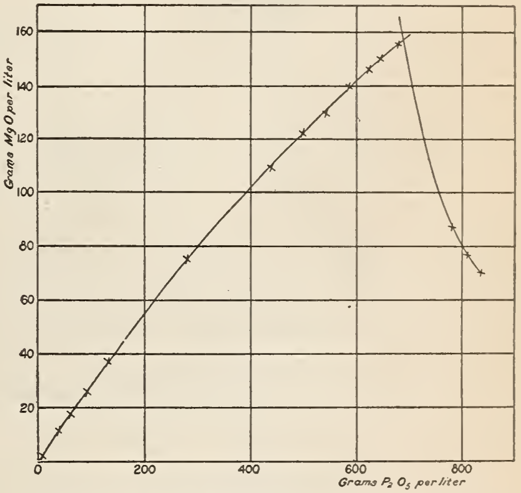

FIG. 4.—Diagram showing the quantities of magnesia and phosphoric acid in solution in equilibrium with the crystalline phosphates of magnesium, at 25°.

PHOSPHATES OF MAGNESIUM.

In an early paper Völcker[a] has shown that water has a very slight solvent action on trimagnesium phosphate. The behavior of magnesium phosphates in contact with water is quite similar to that of the phosphates of lime. It is shown in the following table that there are two series of solutions which exist in contact with the phosphates of magnesia. With the solutions very concentrated with respect to phosphoric acid, the content of magnesia in solution decreases with increasing quantities of phosphoric acid, but with the more dilute solutions both magnesia and phosphoric acid increase regularly. The solid phases were dimagnesium phosphate, in the more dilute solutions and monomagnesium phosphate in the concentrated solutions, at 25° C. The "constant solution" contained about 700 grams of phosphoric acid (P_2O_5) and about 150 grams magnesia (MgO) per liter. The results are given in the following table and diagram (fig. 4). In all but the last three solutions described in the table the solid phase is dimagnesium phosphate, and in the last three monomagnesium phosphate is the stable solid phase.

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[a] Jahresb., 1862, 131.

TABLE XXIV.—*Composition of aqueous solutions containing magnesia and phosphoric acid at 25° C.*

MgO per liter.	P_2O_5 per liter.	Density $\frac{25°}{25°}$.	MgO per liter.	P_2O_5 per liter.	Density $\frac{25°}{25°}$.
Grams.	*Grams.*		*Grams.*	*Grams.*	
0.207	0.486	....	109.5	439.0	....
.280	.732	....	122.6	498.4	1.470
.553	1.917	....	129.9	546.5	....
1.438	4.85	....	140.0	584.0	....
2.23	7.35	1.006	146.8	623.3	1.595
4.73	16.84	1.017	147.3	625.9	....
11.19	38.59	1.042	150.3	645.8	....
17.33	61.21	1.069	155.5	680.7	....
26.09	93.09	1.109	87.1	779.6	1.626
37.40	130.7	1.144	77.1	809.6	1.644
75.5	281.8	1.285	70.6	835.1	1.654

The behavior of trimagnesium phosphate with water containing sulphur dioxide has been investigated by Gerland [a] and by Rotondi.[b] The phosphate was dissolved in the sulphurous acid solution, and after heating the solution the resulting solid which crystallized was a mixture of dimagnesium phosphate and magnesium sulphite. In this respect there is a complete analogy to the action of sulphurous acid upon calcium phosphate.

Völcker [c] has investigated the solvent action of distilled water on trimagnesium phosphate. The ignited phosphate dissolved to the extent of 100 mg. per liter, while the moist precipitated phosphate dissolved to the extent of 205 mg. per liter.

Erlenmeyer [d] has shown that acid citrate solution dissolved trimagnesium phosphate very readily, and neutral citrate solution not so readily.

ACTION OF WATER ON THE PHOSPHATES OF IRON.

The action of water and of aqueous solutions upon the phosphates of iron resembles in a striking manner the action of water and of aqueous solutions upon the phosphates of calcium. There is the same decomposition of the iron phosphates by water, whereby the acid is removed at a different rate from the base, resulting in the formation of a more basic precipitate, and in the formation of a solution which is acid. The preparation of an iron phosphate corresponding in composition to the formula $FePO_4$ is difficult, just as the preparation of a calcium phosphate corresponding to $Ca_3(PO_4)_2$ is difficult.

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[a] Jour. prakt. Chem., **112**, 97 (1871).

[b] Annali di Chimica, **74**, 129 (1882); abstr. in Ber., **15**, 1441 (1882).

[c] Jahresb., 1862, 131.

[d] Ber., **14**, 1253 (1881).

The decomposing action of water upon ferric phosphates has been investigated by Lachowicz.[a] The method of preparation of the iron phosphates used in these experiments was as follows: The precipitate obtained by mixing hot solutions of ferric chloride and disodium phosphate to which ammonia had been added until the solution became neutral was washed with cold water until no chlorine could be detected in the wash water. The analysis of the precipitate was—

48.14 per cent P_2O_5, 48.97 per cent Fe_2O_3.

The formula $FePO_4$ requires,

47.02 per cent P_2O_5, 52.98 per cent Fe_2O_3.

It is apparent that the phosphate employed in these experiments had a greater quantity of phosphoric acid than a phosphate corresponding to the formula $FePO_4$.

Experiment 1: The phosphate was mixed with fifty times its weight of water, allowed to stand for twenty-four hours, and filtered, this operation being repeated ten times. The solution after every filtration was acid to litmus paper, showing that considerable quantities of phosphoric acid had gone into solution, and the solution showed almost no iron by the potassium sulphocyanate test. Analysis of the residue gave:

46.33 per cent P_2O_5, 55.08 per cent Fe_2O_3.

Experiment 2: The phosphate was boiled two or three hours with fifty times its weight of water, filtered, this operation being repeated five times. Analysis of the residue gave:

45.17 per cent P_2O_5, 55.78 per cent Fe_2O_3.

Experiment 3: Repetition of experiment 2. Analysis of this residue gave:

42.56 per cent P_2O_5, 58.49 per cent Fe_2O_3.

Experiment 4: The residue from experiment 3 was washed with hot water until the washings gave no visible precipitate fifteen minutes after ammonia and magnesia mixture had been added. Analysis of the residue gave:

39.82 per cent P_2O_5, 61.98 per cent Fe_2O_3.

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[a] Monatsh., **13**, 357 (1892).

Lachowicz has also investigated the effect of water upon mixtures of a ferric phosphate preparation with freshly precipitated ferric hydroxide. The analyses of the solutions obtained show that water extracts minute quantities of iron and comparatively large quantities of phosphoric acid. The conclusion is drawn that at constant temperature the quantity of ferric phosphate decomposed depends on the quantity of water and the decomposition reaches a limit beyond which it will not go unless the solution is removed and water supplied. In other words, there is a definite equilibrium between the solid and the solution. According to Lachowicz it may happen that with sufficient water all the phosphoric acid can be leached out, leaving only ferric hydroxide.

These results of Lachowicz have been confirmed by Cameron and Hurst,[a] who have also shown that equilibrium conditions are reached quite slowly. In their experiments a ferric phosphate preparation was employed in which there was a considerable excess of phosphoric acid over that required by the formula $FePO_4$. The action of water on the substance can not be considered as one of mere solution only, for if it were a simple solution phenomenon the solution resulting from a mixture of the phosphate and water would have the same composition regardless of the quantity of the solid residue, and if some of the solid remained undissolved the solution would have a definite composition at any definite temperature. This state of affairs, however, does not exist, for not only is the composition of the resulting solution dependent upon the ratio of water to the phosphate, but also the ratio of iron to phosphoric acid is not constant; and if the iron in the solution be considered to be present as $FePO_4$, there is always an excess of free phosphoric acid. In the following tables Cameron and Hurst have shown that the quantity of phosphoric acid in solution is dependent upon the ratio in which the phosphate and water were mixed originally, and also that equilibrium conditions are reached only after many days.

TABLE XXV.—*Iron phosphate in varying quantities of water.*

[Temperature, 25° C. In each case the mixture was allowed to stand one day before an analysis of this solution was made.]

Water per gram of solid.	PO_4 per liter of solution (shaken one minute).	PO_4 per liter of solution (shaken one day).	PO_4 per liter of solution (shaken four days).	PO_4 per liter of solution (shaken seven days).
c. c.	*Gram.*	*Gram.*	*Gram.*	*Gram.*
10	0.214	0.267	0.287	0.320
50	.086	.107	.118	.142
200	.027	.041	.047	.056
800	.010	.013	.016	.020

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[a] Jour. Am. Chem. Soc., 26, 885 (1904).

TABLE XXVI.—*Iron phosphate in varying quantities of water.*

[Temperature, 25° C. Time of contact, 12 days with frequent agitation.]

Water per gram of solid.	PO_4 per liter.	Water per gram of solid.	PO_4 per liter.
c. c.	*Gram.*	*c. c.*	*Gram.*
5	0.512	60	0.152
10	.391	80	.120
20	.283	100	.107
33.3	.215	200	.070
40	.189	400	.042

TABLE XXVII.—*Iron phosphate in varying quantities of water.*

[Temperature, 25° C. Time of contact, 43 days with constant agitation.]

Water per gram of solid.	PO_4 per liter.	Water per gram of solid.	PO_4 per liter.
c. c.	*Gram.*	*c. c.*	*Gram.*
25	0.302	140	0.099
60	.257	200	.080
85	.136	800	.029

TABLE XXVIII.—*Iron phosphate in varying quantities of water.*

[Temperature, 39° C. Time of contact, 16 days with constant agitation.]

Water per gram of solid.	PO_4 per liter.
c. c.	*Gram.*
50	0.269
200	.109
1.000	.033

The concentration of the solution is smaller as the quantity of water originally employed is greater, but the total quantity of material which has gone into solution is greater. This is, of course, to be expected, for the solution in contact with a solid ferric phosphate is less concentrated the greater the proportion of iron to phosphoric acid in the solid.

In another series of experiments Cameron and Hurst have employed a basic phosphate, which contained 70.47 per cent $FePO_4$, 12.37 per cent $Fe(OH)_3$, and 17.16 per cent H_2O. The results show that the action of water is similar in kind to the action of water upon the ferric phosphate which contained an excess of phosphoric acid.

TABLE XXIX.—*Iron phosphate* (*basic*) *in varying quantities of water.*

[Temperature, 25° C.].

Water per gram of solid.	PO_4 per liter of solution.
c.c.	*Gram.*
66.6	0.072
100	.061
200	.037
400	.033

Recent experiments in this laboratory have shown that the phosphates of iron suffer decomposition when treated with water. Solid ferric phosphate, whose composition was not determined, was placed in contact with phosphoric acid solutions of varying concentration. After four months' constant agitation at 25° C. the solutions were analyzed for phosphoric acid and for ferric iron, and the density of the solution also having been determined the percentage of each component could be calculated. The iron was determined as ferrous sulphide by precipitation from the solution which had been made alkaline by an excess of ammonia to dissolve the precipitate formed when the solution is just neutral. The iron was weighed as ferric oxide. Phosphoric acid in the filtrate was determined by precipitation with magnesia mixture. The solid phase was freed as far as possible from the mother liquor, a weighed quantity was dissolved in hydrochloric acid, and aliquot portions were analyzed by the above method for both phosphoric acid and iron. The results of these analyses are given in the following table:

Table XXX.—*Composition of solutions and of residues containing ferric oxide and phosphoric acid at 25° C.*

Solution.			Residue.	
Phosphoric acid, P_2O_5.	Ferric oxide, Fe_2O_3.	Density $\frac{25°}{25°}$	Phosphoric acid, P_2O_5.	Ferric oxide, Fe_2O_3.
Per cent.	*Per cent.*		*Per cent.*	*Per cent.*
0.942	0.0105	1.0074	13.81	15.11
1.984	.0205	1.0162	17.90	19.35
2.838	.0384	1.0244	22.54	23.11
3.770	.0611	1.0310	17.73	15.13
4.706	.0849	1.0383	23.27	20.43

These results are shown on the accompanying diagram (fig. 5). The lines joining the corresponding points are approximately parallel, and hence the solid phase is a solid solution, for it is evident that its composition is continuously variable. The ratio of ferric oxide to phosphoric acid in the limiting solid solution is very close to that represented by $FePO_4$, and if one of these solid solutions be subjected to continual leaching the resulting solid will not be far in composition from $FePO_4$. It will be seen from the table that phosphoric acid is washed from the solid in very much greater quantity than is the iron, and the continual leaching of one of the solid solutions will cause very little loss of iron, but will reduce the phosphoric acid content of the solid very rapidly until the ratio of phosphoric acid to iron is very close to $FePO_4$. Where the solids have considerable acid in excess of $FePO_4$ the amount of iron which will leach out is greater than for smaller excess of acid. This may be seen from the table, for in the last line the phosphoric acid in solution was fifty times as great as ferric oxide, while in the first line the ratio was ninety to one. The fact that the limiting solution does approach so closely in composition to the hypothetical normal ferric phosphate is unquestionably the cause of many of the misconceptions which have arisen in previous studies on the composition and analytical procedures for iron phosphates.

The presence of other salts in such a leaching process undoubtedly alters the conditions materially, as will be seen from the results which follow.

ACTION OF AQUEOUS SOLUTIONS ON THE PHOSPHATES OF IRON.

In the following table of Lachowicz there are given the quantities of phosphoric anhydride and of ferric oxide which have passed into solution under certain well-defined conditions. One liter of the solution was agitated at frequent intervals during 24 hours at ordinary temperature (21° to 26°) with 0.5864 gram of ferric phosphate, the salt solutions containing quantities of salt equivalent to 4 grams of sodium bicarbonate. The determinations were made in duplicate and sometimes in triplicate.

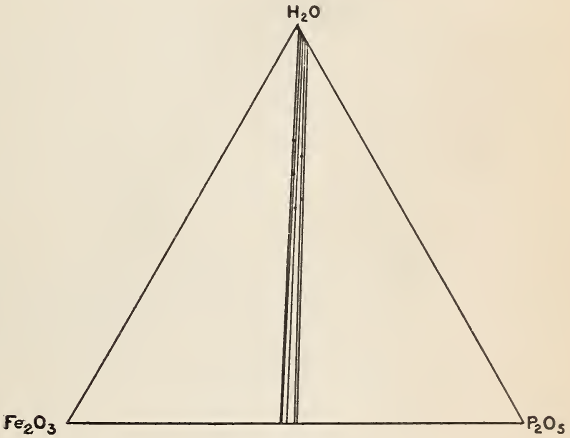

Fig. 5.—Triangular diagram showing the composition of solutions and solid residues for ferric oxide and phosphoric acid, at 25°.

Table XXXI.—*Quantity of ferric oxide and of phosphoric acid dissolved from ferric phosphate by various solutions.*

Salt per liter water.	I.		II.	
	P_2O_5 dissolved.	Fe_2O_3 dissolved.	P_2O_5 dissolved.	Fe_2O_3 dissolved.
	Mg.	*Mg.*	*Mg.*	*Mg.*
Pure water	6.6	2.6	5.4	2.4
Water saturated CO_2	6.2	3.6	5.1	3.9
	6.0	2.8		
4 grams $NaHCO_3$	24.1	4.4	23.7	4.0
5.046 grams Na_2CO_3	297.1	1.6	294.2	2.0
2.284 grams $(NH_4)_2CO_3$	22.2	2.6	23.5	2.1
6.761 grams Na_2SO_4	8.1	1.5	9.1	2.2
6.364 grams $(NH_4)_2SO_4$	6.2	2.1	6.1	1.9
6.476 grams $NaC_2H_3O_2$	14.1	1.6	13.7	2.0
5.624 grams KCl	5.6	2.0	5.9	2.5
4.410 grams NaCl	5.8	2.2	6.0	2.0
4.029 grams NH_4Cl	4.8	3.2	5.4	2.5
	5.1	2.2		
6.464 grams $NaNO_3$	4.5	2.5	5.1	2.9
1.132 grams $CaH_2(CO_3)_2$	6.9	3.5	7.8	3.4

Lachowicz has also determined the quantities of phosphoric acid dissolved by water and solutions from 0.2254 gram of ferric phosphate.

TABLE XXXII.—*Iron phosphate in 80 c.c. water and salt solutions.*

[Temperature, 100° C. Time of contact, 48 minutes.]

Solution.	P_2O_5 dissolved.
	Mg.
Water	9.0
6 per cent K_2SO_4	10.7
6 per cent NH_4Cl	5.2
6 per cent NaCl	6.7

Still other experiments show the action of water and of aqueous solution of ammonium carbonate upon a mixture of ferric phosphate and ferric hydroxide. With 500 c.c. of the solution, there were added 1.1728 grams ferric phosphate and 0.6123 gram ferric oxide as freshly precipitated ferric hydroxide, and the mixture was maintained at 100° C. for one hour. Pure water dissolved 24.3 mg. P_2O_5, and the ammonium carbonate solution (1 gram in 500 c.c.) dissolved 46.5 mg. P_2O_5.

These experiments of Lachowicz indicate that the action of the neutral salts at the concentrations employed was very little different from the action of pure water.[a] The salts giving an alkaline reaction, such as the alkaline carbonates, all showed a marked increase in phosphoric acid content over the phosphoric acid content in neutral solutions or in water.

This is strikingly shown in the case of salt solutions which hydrolyse with the formation of alkaline solutions such as the carbonates or acetates of the alkalis. This action of hydrolyzed bases is most strikingly brought out in the case of disodium phosphate, which markedly increases the solubility of the iron phosphate, although at first thought a decreased solubility might be expected, due to the formation of a common ion. It is common knowledge that solutions of the alkali hydroxides will dissolve iron phosphates, as will also, though less readily, solutions of free mineral acids. This also applies to solutions of salts which hydrolyze with the formation of acid solutions, as is shown by the experiments of Schneider,[b] in which it was found that the solubility of iron phosphate is increased by the presence of the chloride or sulphate of iron, both of which yield end solutions.

Gerlach[c] found that oxalic acid was a more effective solvent than citric acid, which in turn was much more effective than acetic acid;

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[a] The early work of Luna (Heiden's Lehrbuch der Düngemittel, 2d edn., p. 494) that the presence of sodium, potassium, and ammonium salts increases the solubility of iron phosphate is not confirmed in many cases by the more recent researches.

[b] Zeit. anorg. Chem., **5**, 84; **7**, 386 (1894).

[c] Landw. Vers.-Stat., **46**, 201 (1895).

in the presence of an excess of free iron hydroxide the solvent action of oxalic acid was unaffected, while that of citric acid was much lowered, and acetic acid did not dissolve enough phosphoric acid to be detected. Lachowicz studied the action of humic acid (?), but his experimental results hardly warrant his conclusion that this substance increases the solubility of iron phosphate, since the observed effects were more probably due to the free bases, also present in the solution as a result of the hydrolysis of the supposed humates. His experiments at 100° C. show, as might be expected, that temperature has a large influence on hydrolysis, but they also are unsatisfactory on account of the time element.

The following tables contain the results of Cameron and Hurst upon the action of aqueous solutions of various alkali salts upon iron phosphate. The preparation of the iron phosphate used in the first three of these tables contained an excess of phosphoric acid over $FePO_4$, and the preparation used in the last table contained a considerable excess of ferric oxide over $FePO_4$.

Table XXXIII.—*Iron phosphate in solutions of sodium nitrate.*

[Temperature, 25° C. Time of contact, 40 days, with constant agitation.]

Quantity of solution added to 1 gram solid ferric phosphate.	$NaNO_3$ per liter.	PO_4 dissolved per liter.
	Grams.	*Gram.*
20 cubic centimeters	0	0.3500
	5	.2237
	25	.1912
	75	.1622
	150	.1451
	300	.1084
40 cubic centimeters	0	.2175
	5	.1786
	25	.1558
	75	.1331
	150	.1124
	300	.0776
100 cubic centimeters	0	.1250
	5	.1130
	25	.0976
	150	.0615
	300	.0482

TABLE XXXIV.—*Iron phosphate in solutions of potassium chloride.*

[Temperature, 25° C.]

Quantity of solution added to 1 gram solid ferric phosphate.	KCl per liter.	PO_4 dissolved per liter.	Fe dissolved per liter.
	Grams.	*Gram.*	*Gram.*
20 cubic centimeters	0.0	0.3500	....
	.111	.2256	....
	.272	.2011	....
	.444	.1689	....
	5.0	.1127	0.0429
	25	.0905	.0480
	75	.0820	.0540
	150	.0871	.1020
	300	.0871	.1420
40 cubic centimeters	0.0	.2175	.0152
	5.0	.0930	.0152
	25	.0769	.0168
	75	.0569	.0200
	150	.0528	.0320
	300	.0428	.0700
100 cubic centimeters	0.0	.1250	....
	5.0	.0602	.0128
	25	.0448	.0144
	75	.0374	.0168
	150	.0314	.0248
	300	.0268	.0376

TABLE XXXV.—*Iron phosphate in solutions of potassium sulphate.*

[Temperature, 25° C. Time of contact, 19 days.]

Quantity of solution added to 1 gram solid ferric phosphate.	K_2SO_4 per liter.	PO_4 dissolved per liter.
	Grams.	*Gram.*
20 cubic centimeters	3	0.320
	6	.344
	25	.366
	50	.372
	75	.367
	150	.364

TABLE XXXVI.—*Iron phosphate (basic) in solutions of potassium chloride.*

[Temperature, 25° C. Time of contact, 15 days, with constant agitation.]

Quantity of solution added to 1 gram solid ferric phosphate.	KCl per liter.	PO_4 dissolved per liter.
	Grams.	*Gram.*
200 cubic centimeters	0	0.037
	3	.011
	5	.009
	15	.012

The solutions of which the concentration in phosphoric acid has been given in Tables XXXIII, XXXIV, and XXXV were titrated against a known solution of alkali and the results showing the acidity of these solutions by this method have been recorded. In all these cases the quantity of phosphoric acid contained in solution falls off rapidly as the concentration with respect to the neutral salt is increased, or else as in the case of potassium sulphate solutions the phosphoric acid content increases slightly with increasing quantities of potassium sulphate in solution. In all cases the acidity, as is shown by titration, increases markedly as the concentration of the neutral salt increases. It does not seem probable that this acidity can be ascribed solely to phosphoric acid in solution, for the acidity increases markedly while the quantity of phosphoric acid either decreases or else remains nearly constant. It would, therefore, seem that there is some change effected in the neutral salt, possibly a selective absorption,[a] whereby the basic part unites with the solid residue, leaving free acid in solution.

The organic matter in soils, usually known as humic acid, is considered by Lachowicz to possess a distinct solvent action upon ferric phosphate. This conclusion is based on the observation that a solution containing sodium bicarbonate or ammonium carbonate and the humic acid will dissolve more phosphoric acid and ferric oxide from a ferric phosphate than will a solution containing the carbonate alone. Lachowicz's results are as follows:

TABLE XXXVII.—*Iron phosphate in carbonate solutions with and without humic acid.*[a]

In 1 liter solution.	Ferric phosphate used.	P_2O_5 in solution.	Fe_2O_3 in solution.
	Gram.	*Gram.*	*Gram.*
4 grams $NaHCO_3$	0.5864	0.0241	0.0044
		.0237	.0040
4 grams $NaHCO_3$ + 0.1724 gram humic acid	.5864	.0243	.0055
		.0257	.0059
25 drops 10 per cent solution $(NH_4)_2CO_3$	.5864	.0190	.0029
		.0182	.0021
25 drops 10 per cent solution $(NH_4)_2CO_3$ + 0.431 gram humic acid	.5864	.0227	.0081
		.0212	.0083

[a] Gesteins- und Bodenkunde, p. 329 (1877).

The results in this table indicate that solutions carrying humates and carbonates have a greater effect upon iron phosphate than a solution carrying the carbonate alone. These effects may have been due to the free bases in solution as a result of the hydrolysis of the supposed humates, an explanation in harmony with the work of Schneider[b] upon the action of alkaline solutions of humus upon iron phosphates.

In a preceding table Lachowicz has shown that this effect of water upon the iron phosphates was decreased by an excess of iron hydroxide. Saturating the water with carbon dioxide produced no appreciable effect in its action upon iron phosphate. This observation was confirmed by Gerlach[c], who found further that, when calcium carbonate was mixed with either iron or aluminum phosphate in water, carbon dioxide caused an increased amount of calcium to go into solution without producing any noticeable effect upon the amount of dissolved phosphoric acid. It has been found, however, that calcium carbonate and especially the bicarbonate does increase the solubility, and Sutherst,[a] while holding that calcium carbonate has little or no value, states that lime in the form of hydroxide does increase the solubility of the phosphates of iron and aluminum.[b]

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[a] See Bul. No. 30, Bureau of Soils, U. S. Dept. Agr. (1905).

[b] Zeit. anorg. Chem., **5**, 84; **7**, 386 (1894).

[c] Landw. Vers.-Stat., **46**, 201 (1895).

The effect of various solutions upon ferric phosphate has been determined in this laboratory. Five grams of ferric phosphate was shaken for five days with 100 c. c. water and with 100 c. c. of solution saturated with carbon dioxide, gypsum, and lime. The following quantities of phosphoric anhydrite were found in solution: In water, 74 mg.; in saturated carbon dioxide solution, 171 mg.; saturated gypsum solution, 118 mg., and in saturated lime solution, 0.0 mg.

ACTION OF WATER ON THE PHOSPHATES OF ALUMINA.

The literature upon the subject of the action of water and of solutions upon the phosphates of alumina is very small. It has been stated that it behaves similarly to ferric phosphate, but was less resistant to the action of water or saline solutions. The presence of carbon dioxide in the solution appears to have no appreciable effect upon the amounts of alumina or phosphoric acid dissolved even when lime or magnesia is present.[c] The solubility of aluminum phosphate is increased by the hydroxides of potassium or sodium, and to a lesser extent by free mineral acids. Oxalic and citric acids were about equally effective, and much more so than acetic acid in bringing phosphoric acid into solution. Free aluminum hydroxide, while greatly reducing the action of acetic acid, did not affect that of the oxalic or citric acids. Schneider[d] states that the solubility is increased by aluminum chloride or aluminum sulphate, which substances themselves give acid solutions.

The action of water upon various preparations of aluminum phosphate has been studied by Cameron and Hurst.[e] Their results are reproduced in the following tables:

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[a] Chem. News, **85**, 157 (1902); Agr. Gaz., **55**, 204 (1902).

[b] It seems to be held by many agricultural writers that lime increases the solubility of the iron phosphate of the soil, since liming is often beneficial in producing increased plant growth. It is greatly to be regretted, however, that instead of accepting a conclusion on indirect evidence these authors have not seen fit to investigate the problem in the only way in which it can be attacked—i. e., by direct experiment. In this way erroneous statements as to the phosphates would be avoided, and a truer view of the function of liming might be gained.

[c] Gerlach, Landw. Vers.-Stat., **46**, 201 (1895).

[d] Zeit. anorg. Chem., **5**, 87 (1894).

[e] Jour. Am. Chem. Soc., **26**, 385 (1904).

TABLE XXXVIII.—*Aluminum phosphate (Al, 21.49 per cent; PO_4, 77.42 per cent) in varying quantities of water.*

[Temperature, 25°. Time of contact, 21 days, with constant agitation.]

Water per gram solid.	PO_4 per liter.	Water per gram solid.	PO_4 per liter.
C. c.	*Gram.*	*C. c.*	*Gram.*
25	0.6789	425	0.0589
75	.2477	800	.0343
175	.1172		

TABLE XXXIX.—*Aluminum phosphate, as above, in varying quantities of water.*

[Temperature, 25°. Time of contact, 48 days, with constant agitation.]

Water per gram solid.	PO_4 per liter.	Al per liter.	Water per gram solid.	PO_4 per liter.	Al per liter.
C. c.	*Gram.*	*Gram.*	*C. c.*	*Gram.*	*Gram.*
50	0.3886	0.0359	600	0.0516	0.0065
100	.2110	.0157	4,000	.0113	.0033
250	.0068	.0079	8,000	.0049	....

TABLE XL.—*Aluminum phosphate, as above, in varying proportions of water.*

[Temperature, 35°. Time of contact, 30 days, with constant agitation.]

Water per gram solid.	PO_4 per liter.
C. c.	*Gram.*
25	0.889
50	.503
100	.274
200	.131

TABLE XLI.—*Aluminum phosphate (Al, 21.16 per cent; PO_4, 81.33 per cent) in varying proportions of water.*

[Temperature, 30°. Time of contact, 35 days, with constant agitation.]

Water per gram solid.	PO_4 per liter.
c. c.	*Gram.*
20	0.241
40	.134
80	.081

TABLE XLII.—*Aluminum phosphate (Al, 19.82 per cent; PO_4, 78.79 per cent) in varying proportions of water.*

[Temperature, 25°. Time of contact, 15 days, with constant agitation.]

Water per gram solid.	PO_4 per liter.
c. c.	*Gram.*
66.7	0.0039
100	.0037
200	.0035
400	.0039

The results in the above tables indicate that the total quantity of phosphoric acid which passes into solution increases with increasing quantities of water, but that the concentration of the solution decreases considerably as the quantity of water increases. It is also shown in one case, where the aluminum content of the solution was determined, that the aluminum content of the solution was much less than the equivalent of the phosphoric acid, and hence there is a change in the solid as leaching continues, whereby the solid becomes richer in alumina.

ACTION OF SOLUTIONS ON THE PHOSPHATES OF ALUMINA.

The effect of various aqueous solutions upon the quantity of phosphoric acid passing into solution under various conditions has also been determined by Cameron and Hurst, and their results are quoted in the following tables:

TABLE XLIII.—*Aluminum phosphate (Al, 21.49 per cent; PO_4, 77.47 per cent) in aqueous solutions of potassium chloride; one gram phosphate in 100 c. c. solution.*

[Temperature, 30°. Time of contact, 30 days, with constant agitation.]

KCl per liter solution.	PO_4 per liter solution.
Grams.	*Gram.*
0	0.287
5	.270
35	.266
125	.249

TABLE XLIV.—*Aluminum phosphate (Al, 21.26 per cent; PO_4, 81.33 per cent) in aqueous solutions of potassium chloride.*

[Temperature, 27°. Time of contact, 27 days, with constant agitation.]

1 gram solid to 20 c. c. solution.		1 gram solid to 80 c. c. solution.	
KCl per liter.	PO_4 per liter.	KCl per liter.	PO_4 per liter.
Grams.	*Gram.*	*Grams.*	*Gram.*
0	0.241	0.0	0.081
150	.201	2.5	.071
200	.189	17.2	.067
250	.186	60.9	.065

TABLE XLV.—*Aluminum phosphate (Al, 19.82 per cent; PO_4, 78.79 per cent) in aqueous solutions of potassium chloride; 1 gram solid in 200 c. c. solution.*

[Temperature, 25°. Time of contact, 15 days, with constant agitation.]

KCl per liter.	PO_4 per liter.
Grams.	*Gram.*
0	0.0035
5	.0031
15	.0033

In the above tables it will be noticed that the aluminum phosphates act similarly to those of iron and lime in respect to their behavior with aqueous solutions of potassium chloride. As the concentration of the chloride increases the quantity of phosphoric acid in the solution decreases regularly. Potassium sulphate and sodium nitrate also show the same effect, as will be brought out in the following tables:

TABLE XLVI.—*Aluminum phosphate (Al, 21.16 per cent; PO_4, 81.33 per cent) in aqueous solutions of potassium sulphate.*

[Temperature, 35°. Time of contact, 10 days, with constant agitation.]

One gram solid to 20 c. c. solution.		One gram solid to 80 c. c. solution.	
K_2SO_4 per liter.	PO_4 per liter.	K_2SO_4 per liter.	PO_4 per liter.
Grams.	*Gram.*	*Grams.*	*Gram.*
0.0	0.241	0.0	0.080
5.4	.218	2.5	.071
49.0	.191	7.7	.068
101.4	.183	27.2	.064
		62.5	.062

TABLE XLVII.—*Aluminum phosphate, as above, in aqueous solutions of sodium nitrate.*

[Temperature, 27° C. Time of contact, 15 days, with constant agitation.]

One gram solid to 20 c. c. solution.		One gram solid to 80 c. c. solution.	
$NaNO_3$ per liter.	PO_4 per liter.	$NaNO_3$ per liter.	PO_4 per liter.
Grams.	*Gram.*	*Grams.*	*Gram.*
0	0.3094	0.0	0.0811
20	.2988	2.5	.0807
60	.2818	7.5	.0798
140	.2732	17.5	.0794
240	.2220	27.5	.0790
		87.5	.06547

Aluminum phosphate is similar to iron phosphate, in that neutral salts affect its solubility to a far less extent than do solutions which are acid or alkaline.

SUMMARY.

In this bulletin it has been shown that the soil phosphates are decomposed or hydrolyzed by water, with the formation of other phosphates containing relatively more of the base.

Neutral salts in solution have a marked effect upon the amount of phosphoric acid and of lime going into solution from a lime phosphate, generally increasing both. Lime salts generally decrease the amount of both in solution, as do alkaline solutions, while acid solutions increase it.

Neutral salts have, however, little effect upon the solubility of the phosphates of iron or alumina, and it is impossible to predict the direction of the effect. Salts which hydrolyze with the formation of acid or alkaline solutions increase the amount of phosphoric acid yielded to the solution by the phosphates of iron and alumina.

The phosphates of the soil, whether solid solutions or definite chemical compounds, are of such a nature as to yield a solution containing very small quantities of phosphoric acid. Inasmuch as all soils contain far more basic matter than is sufficient to combine with the phosphoric acid, the least soluble phosphates are the ones which will be formed and will control the concentration of the soil moisture. This fact, together with the well-known phenomena of absorption, gives a satisfactory explanation of the observation that the concentration of the soil moisture is low and varies but little for different soils and with the total amount of phosphoric acid in the soils. For the same reason, the addition of phosphatic fertilizers can not be expected to influence materially the concentration of phosphoric acid in the soil moisture.

The action of phosphatic fertilizers is, therefore, on the soil and not primarily on the plant; for the concentration in plant food constituents of the solution on which the plant feeds is not materially altered by the addition of phosphatic fertilizers in the amounts used in ordinary field practice.

The changes in both solution and solid which take place during the progress of leaching superphosphates have been described.

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